Angewandte Chemie
GDCh
Eine Zeitschrift der Gesellschaft Deutscher Chemiker
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Zitierweise: *Angew. Chem. Int. Ed.* 10.1002/anie.202004892

Link zur VoR: https://doi.org/10.1002/anie.202004892

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Holey Lamellar High Entropy Oxide as Ultra-Highly Active Heterogeneous Catalyst for Solvent-free Aerobic Oxidation of Benzyl Alcohol

Danyang Feng,[a] Yangbo Dong,[a] Liangliang Zhang,[a] Xin Ge,[b] Wei Zhang,[b] Sheng Dai,[c] and Zhen-An Qiao*[a]

Abstract: The development of noble metal free heterogeneous catalysts is promising for selective oxidation of aromatic alcohols; however, the relatively low conversion of non-noble metal catalysts under solvent-free atmospheric condition greatly restricts their industrial application. Herein, we designed synthesize a novel holey lamellar high entropy oxide (HEO) $Co_{0.2}Ni_{0.2}Cu_{0.2}Mg_{0.2}Zn_{0.2}O$ material with mesoporous structure via a simple anchoring and merging process. The prepared holey lamellar HEO as heterogeneous catalyst exhibits ultra-high catalytic activity for the solvent-free aerobic oxidation of benzyl alcohol. Up to 98% conversion can be achieved in only 2 hours, to our knowledge, it is the highest conversion of benzyl alcohol oxidation reaction so far. By rational regulating the catalytic reaction parameters, benzoic acid or benzaldehyde can be selectively optimized as the main product. Multiple analytical characterizations and theory calculation provide a deeper insight into the catalysis mechanism, revealing the synergistic effect of the unique HEO material, abundant oxygen vacancies and holey lamellar framework leads to the ultra-high catalytic activity.

Introduction

Selective oxidation of benzyl alcohol to produce benzaldehyde, benzoic acid and benzyl benzoate is of great significance in both laboratory research and industrial applications. Benzaldehyde and benzoic acid are valuable intermediates in industrial manufacture, and benzyl benzoate are key commercially raw materials for fine chemical engineering. Recently, homogeneous catalysts have been confirmed to be effective in selective oxidation of alcohols in the presence of organic solvents or under high pressures.[1-4] However, in the viewpoint of sustainable and green chemistry, the hazardous organic solvents or hydroperoxides agents used in homogeneous catalysis easily lead to environmental pollution problems. Besides, the high-pressure condition needed in homogeneous catalysis place high demands on catalytic equipment, consumes more energy and are prone to safety risks. The ideal catalysts are supposed to be workable without any solvents or oxidizing agents in atmospheric conditions. Compared with homogeneous catalysts, heterogeneous catalysts have the merits of environmental benign, facilitating separation and recycle. Therefore, the construction of green and highly active heterogeneous catalysts for the solvent-free aerobic oxidation of benzyl alcohol is highly demanded. Recently, tremendous efforts have been made to study noble metals heterogeneous catalysts, such as Pt- and Pd-based catalysts, due to their satisfactory catalytic activity.[5-9] Nevertheless, taking into account the exorbitant price and finite reserves of noble metals, non-noble metals heterogeneous catalysts have a broader application prospect in the catalytic field.

Transition metal oxides, as a class of low-cost and resource-rich materials, have been widely employed as catalysts in various types of catalytic processes, such as the aerobic oxidation of primary carbon hydrogen bonds, alcohols and amines.[10-12] For instance, Chen et al. reported that Co nanoparticles encapsulated inside nitrogen-rich carbon exhibited extraordinary efficiency in catalytic oxidation of alcohols to esters.[13] Zhao et al. found that magnetic mesoporous TiO_2 showed excellent catalytic performance as a sonocatalyst for the degradation of bisphenol-A.[14] Compared with simple metal oxides, the synergistic interactions among multiple types of catalytic active sites in complex metal oxides make them exhibit higher catalytic activity. For example, $Zn_4Co_1O_x$@carbon hollow particles showed superior performance for the hydrogenation of nitrobenzene to aniline.[15] Multi-metallic catalyst CeO_2–Co_3O_4 hybrids exhibited remarkable synergistic effect in the chemical reduction of NO by CO.[16] Thus, rational designing transition metal oxide heterogeneous catalysts equipped with multiple catalytic sites are of great value in applied catalysis area, but it still suffers from the much lower catalytic activity than that of noble ones at present.

Among the majority of complex metal oxides, high entropy oxides (HEO), defined as five or more near-equimolar metal elements arranged deliberately in a single-phase lattice with randomized distribution, have attracted ever-increasing attention because of their diverse redox behavior, abundant cation compositions, exceptional chemical and thermal stability.[17-19] The multi-electron redox properties in HEO make it a potential high-performance catalyst for organic reaction. The most common approaches to synthesize HEO are arc-melting and spark plasma sintering methods under ultrahigh temperature.[20] However, limited by the current high temperature synthetic conditions, the obtained micron-sized HEO grains expose only a small portion of the effective catalytic sites, which greatly restricts their catalytic performance. From this point of view, the synthesis of HEO catalyst with porous framework composed of self-linked HEO small nanoparticles will satisfy the requirement of catalytic reaction and provide opportunities for boosted catalytic activity.

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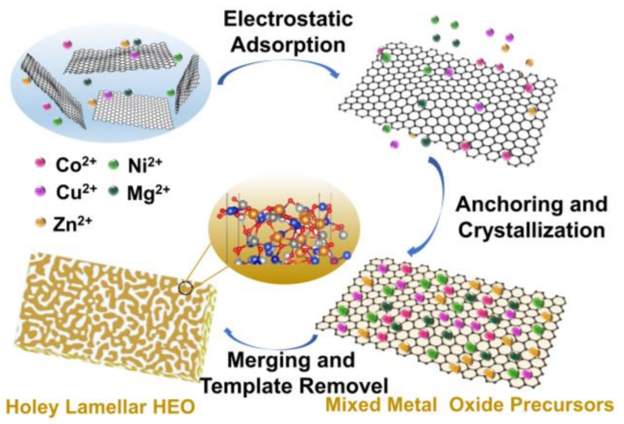
10.1002/ange.202004892

Herein, holey lamellar HEO material $Co_{0.2}Ni_{0.2}Cu_{0.2}Mg_{0.2}Zn_{0.2}O$ is designed and synthesized for the first time by an anchoring-merging process using graphene oxide (GO) as a sacrificial template. The metal ions are firstly absorbed on the surface of GO by electrostatic interaction and the pinning forces between metal precursors and GO template effectively prevent the agglomeration of the small precursor nanoparticles in the heating process, then the metal precursors merge into high-entropy structure with single phase under high temperature. The obtained holey lamellar HEO as heterogeneous catalyst exhibits ultra-high catalytic activity for the solvent-free aerobic oxidation of benzyl alcohol. Remarkably, up to 98% conversion is achieved in only 2 hours, which is the highest conversion of benzyl alcohol reported so far. The unique structure of elements randomly distributed on the atomic scale endows the HEO material unexpected catalytic properties, and the holey lamellar structure composed of numerous HEO nanoparticles greatly increases surface exposure of the catalytic sites and makes the catalyst rich in oxygen vacancies. Density functional theory (DFT) calculations declare that the presence of oxygen vacancies significantly increases the adsorption energies of holey lamellar HEO material for benzyl alcohol. What's more, the effect of various key parameters in the catalyzing process are further explored, and the main product can be selectively optimized as benzoic acid or benzaldehyde by rational regulating the component of the catalyst and the catalytic reaction time. These findings suggest that HEO materials have broad application prospects in the field of industrial catalysis.

Results and Discussion



Scheme1. Schematic illustration of the formation process for holey lamellar HEO material ($Co_{0.2}Ni_{0.2}Cu_{0.2}Mg_{0.2}Zn_{0.2}O$).

As shown in Scheme 1, the liquid phase system using ethylene glycol as a solvent ensures that the metal ions are highly dispersed at molecular level. GO modified with negatively charged oxygen-containing functional groups is employed as two-dimensional substrate, and the electrostatic interaction promotes the five individual positively charged metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}) to adsorb and stabilize uniformly onto the surface of GO template (Figure S1). As the calcination temperature rises, the precursor nanoparticles are firmly fixed to GO and the pinning forces between metal precursors and GO hinder the diffusion and agglomeration of these nanoparticles.[21] Meanwhile, the amorphous precursors transform into crystalline mixed metal oxides nanocrystals and these nanocrystals self-link with each other to form holey lamellar structure. Further treating the sample in an air atmosphere at 900 °C, the GO template is completely burned off and the mixed metal oxides merge into single crystal phase with high entropy structure, simultaneously the holey structure can be well maintained. As shown in Figure S2, the more the metal source is added, the larger the HEO particle size is obtained.

The transmission electron microscopy (TEM) image of the holey lamellar HEO was shown in Figure 1a. The interconnected HEO nanoparticles forms the wall of the holey structure and the average particle size is estimated to be 8-12 nm, as illustrated by aberration-corrected scanning transmission electron microscopy (STEM) image (Figure 1b). The atomistic crystal structure of the holey lamellar HEO was shown in Figure 1c, the interlayer spacing of 0.241 nm in HRTEM was indexed to the (111) crystal plane of HEO phase. To characterize the spatial distribution of elements in holey lamellar HEO, energy-dispersive spectroscopy (EDS) elemental mapping (Figure 1d and 1e) and ICP analysis (Table S1) were conducted, which evidenced that Co, Ni, Cu, Mg, Zn and O were uniformly distributed over the whole detection range.

X-ray diffraction (XRD) characterization of holey lamellar HEO was conducted to verify the structural information. As shown in Figure 1f, a series of multiphase mixture peaks are presented after pyrolyzed at 500 °C, among which an obvious peak of graphitic carbon is observed at 26° (2θ), belonging to the incomplete combustion of GO substrate. Subsequently further increasing the calcination temperature to 900 °C, the carbon is completely removed and the multiphase mixture transform to face-centered cubic (FCC) single-phase, demonstrating the multiphase metal oxides transform to HEO phase. The average HEO particle size is about 11.2 nm calculated by the Scherrer formula according to the XRD pattern, which is in accordance with the TEM observation. The diffraction peaks at 2θ values of 36.7, 42.6, 61.9, 74.2 and 78.1º are attributed to the (111), (200), (220), (311) and (222) lattice planes, respectively.[22] Then the HEO material is re-calcined under 750 °C, the single-phase transforms back to multiphase, and this kind of structural reversibility is a key feature of entropy-driven transition, further confirming the high entropy structure.[17] The specific surface area and pore volume of holey lamellar HEO are 42 $m^2 \cdot g^{-1}$ and 0.106 $cm^3 \cdot g^{-1}$, respectively. As shown in Figure 1g, holey lamellar HEO exhibits a typical IV curve with a H_1-type hysteresis loop. The increase in the adsorption band at $P/P_0 = 0.7-0.9$ confirms the formation of mesoporous architecture, which comes from the self-linked small HEO nanoparticles.

Aerobic oxidation of aromatic alcohols by using efficient and economic complex transition metal oxides catalysts has great potential in industrial catalytic applications.[23-25] Herein, the as-prepared holey lamellar HEO was employed as heterogeneous catalyst for solvent-free aerobic oxidation of benzyl alcohol (Figure 2a). The catalytic activity of the catalyst is evaluated in the oxidation of neat benzyl alcohol under atmospheric condition. In the absence of catalyst, the conversion of benzyl alcohol is lower than 1%. Encouragingly, with the addition of the holey lamellar

HEO catalyst, the catalytic conversion increases exponentially with increasing reaction temperature from 100 °C to 120 °C (Table S2), and up to 98% conversion can be achieved after reaction at 120 °C for only 2 hours under solvent-free atmospheric conditions. To our best knowledge, this is the highest conversion among previous reported single atom, clusters, noble metal and alloy catalysts in literatures (Figure 2b and Table S3).[26-33] It should be pointed out that the TOF numbers in literature were calculated on the basis of loading amount of noble metals (loading rate=0.5 wt%-5 wt%), and the metal oxides are just work as supports not catalytic active materials. However, noble metals do not exist in this catalytic system, and the TOF value can only be calculated to be 994 in terms of the amount of HEO. Au/Pd-TiO_2 catalyst, whose conversion is 91.6% in 8 hours under 0.2 MPa of O_2, is the most advanced catalyst ever reported.[26] Compared with Au/Pd-TiO_2 catalyst, the holey lamellar HEO catalyst not only works at atmospheric pressure, but also reaches the equilibrium of the catalytic reaction in less time. There are three products in this oxidation process: benzaldehyde, benzoic acid and benzyl benzoate. Benzoic acid is the dominant product in the catalytic reaction, benzaldehyde and benzyl benzoate are identified as the major byproducts. In the reaction process, the benzyl benzoate is formed by the esterification of benzyl alcohol with benzoic acid. As a comparison sample, the bulk HEO (Figure S3) catalyst under the same catalytic condition shows a fairly low catalytic activity with the conversion of only 6%, confirming the unique holey lamellar structure plays a crucial role in the excellent catalytic performance of HEO materials. The recyclability and stability of holey lamellar HEO catalyst on benzyl alcohol are further evaluated. After 5 cycles, the selectivity and conversion are almost the same as that of the fresh catalyst, indicating the catalyst is highly stable in the catalytic environment.

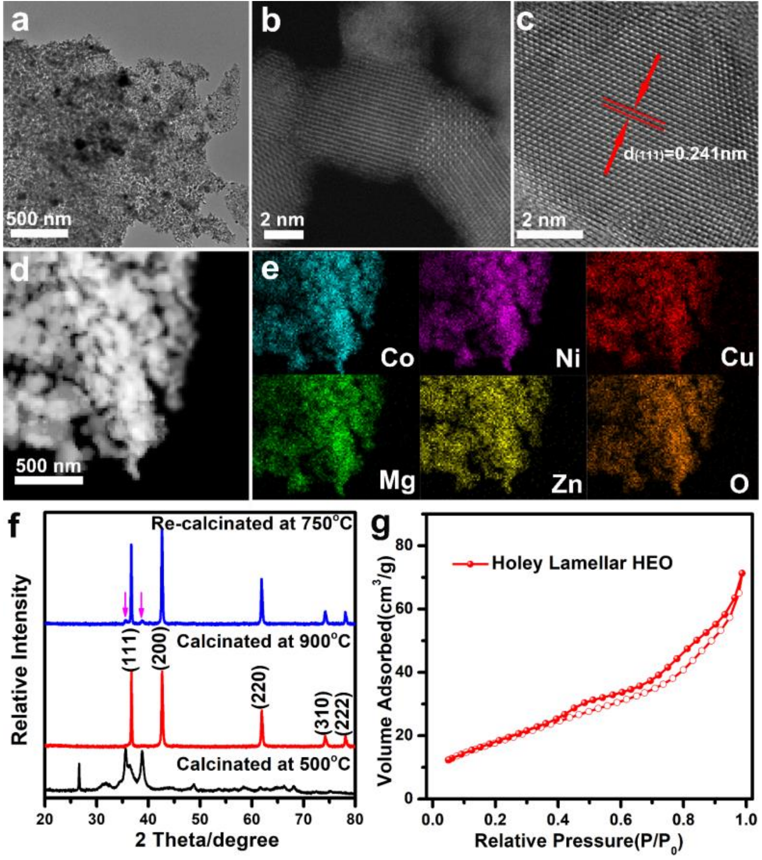


Figure 1. Characterization of holey lamellar HEO. (a) TEM and (b, c) HRTEM images of holey lamellar HEO. (d) and (e) Elemental mapping images of holey lamellar HEO. (f) XRD patterns of holey lamellar HEO calcined at different calcination temperature and (g) N_2 sorption isotherms of holey lamellar HEO.

To demonstrate the general applicability of our holey lamellar HEO catalyst, catalytic experiments on benzyl alcohol derivatives were carried out. As shown in Figure 2c, holey lamellar HEO shows decent catalytic oxidation performance for the derivatives compared to other heterogeneous catalysts, though the conversion is not as high as that of benzyl alcohol. The catalytic activity is closely related to the substituent group linked with benzyl alcohol. For electron-donating derivatives, such as methylbenzyl alcohol or methoxy benzyl alcohol, the selectivity to corresponding aldehyde is obviously improved (over 50%). The reduced catalytic conversion is assigned to the high steric hindrance effect of the substituents impeding the dehydrogenation in the catalytic reaction. For electron-withdrawing derivatives, such as nitro-benzyl alcohol, the catalytic activity is almost the same as the blank test, and this extremely low conversion is attributed to the synergistic effect of steric hindrance and catalytic inhibition of the nitro substituents.

The FT-IR spectra was used to confirm the oxidation process of oxidation of benzyl alcohol. As shown in Figure 2d, the peaks at 1020 cm^{-1} and 1369 cm^{-1} is assigned to the stretching vibrations of (C-OH) and (O-H) in benzyl alcohol, respectively. After reaction for 0.2 hour, a new peak at 1689 cm^{-1} belonged to (C=O) group in benzaldehyde is observed and this peak shifts towards higher wavenumbers as the benzaldehyde is over oxidized to benzoic acid and benzyl benzoate in the following oxidation process. When the catalytic reaction proceeds to 0.5 hour, two additional peaks located at 2855 cm^{-1} and 2926 cm^{-1} appear, which are the characteristic absorption peaks of saturated methyl and methylene in benzyl benzoate, demonstrating the esterification between benzyl alcohol and benzoic acid. The step-by-step-oxidation process of benzyl alcohol confirmed by infrared is consistent with our previous speculation. The evolution of catalytic substrate with reaction time in the oxidation reaction is shown in Figure 2e. When benzyl alcohol is used as catalytic substrate, the reaction rate is too fast to monitor, so 4-methylbenzyl alcohol, whose oxidation process is easier to detect, is chosen as the substrate. The evolution process of 4-methylbenzyl alcohol further proves that the catalysis of aromatic alcohol follows the rule of stepwise oxidation.

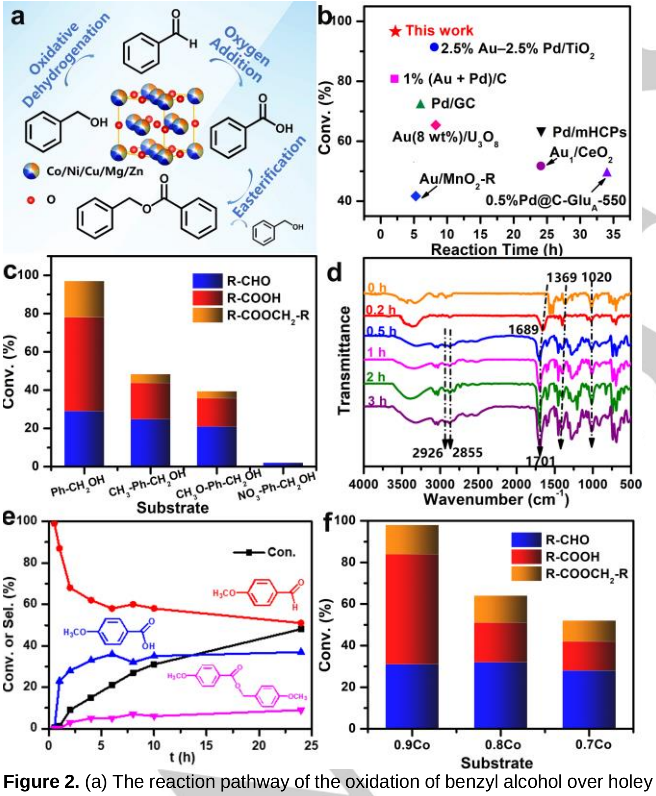
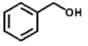
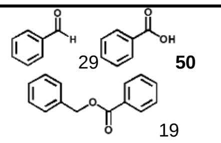
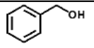
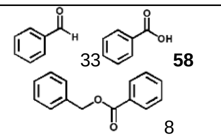
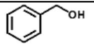
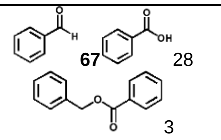
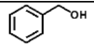
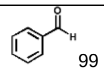
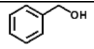
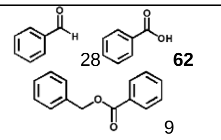
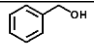
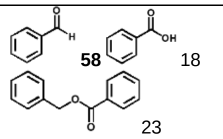
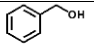


Figure 2. (a) The reaction pathway of the oxidation of benzyl alcohol over holey lamellar HEO catalyst. (b) Comparison of the catalytic conversion of holey lamellar HEO catalyst with those reported in the literatures (2.5%Au–2.5%Pd/TiO$_2$,[26] Pd/GC,[27] Au/MnO$_2$-R,[28] Au$_1$/CeO$_2$,[29] Pd/mHCPs,[30] Au(8 wt%)/U$_3$O$_8$,[31] 1% (Au+Pd)/C,[32] 0.5%Pd@C-Glu$_A$-550,[33]). (c) Catalytic performance of holey HEO in benzyl alcohol, methylbenzyl alcohol, methoxy benzyl alcohol and nitro-benzyl alcohol oxidation. (d) FT-IR spectra of the benzyl alcohol evolution as a function of reaction time. (e) The time–activity profile for 4-methoxy benzyl alcohol oxidation under aerobic conditions. (f) Catalytic performance of Co element is reduced by 10%, 20% and 30%, separately.

Due to HEO is a kind of unique solid solution composed by five nearly equimolar metal elements, the study on the influence of each element content on catalytic performance is carried out in the premise of not changing the holey lamellar structure (Figure 2f). When the content of each metal element is reduced by 10% separately, except the time reaching chemical equilibrium is prolonged to nearly 3 hours, there is no obvious change in the conversion and selectivity under the same catalytic condition (Figure S4), and the corresponding XRD pattern of the catalysts does not show any changes either. (Figure S5). Whereas further reducing the content of each metal element by 30% separately, the reaction time for reaching chemical equilibrium is dramatically prolonged to 14 hours, and the catalysts exhibit obviously increased selectivity of over 50% towards benzaldehyde (Figure S6). However, compared with holey lamellar HEO catalyst, the catalytic conversion drops by nearly half, and the peak positions of the catalysts in the XRD pattern also changes (Figure S7). These results demonstrate that the specific single-phase HEO material and the unique holey lamellar structure are both indispensable for catalytic performance. In light of these results, by regulating the component of the catalyst and the catalytic reaction time, we can optimize benzoic acid or benzaldehyde as the main product of benzyl alcohol oxidation, respectively. The corresponding catalysis results are shown in Table 1.

Table 1. Solvent-free aerobic oxidation of benzyl alcohol over various catalysts.

Catalyst	Substrate	Product Sel.(%)	t(h)	Conv.(%)
Holey HEO		 29 **50** 19	2	98
Holey HEO		 33 **58** 8	1	73
Holey HEO		 **67** 28 3	0.5	49
bulk HEO		 99	24	6
Holey HEO (0.9Ni)		 28 **62** 9	2	89
Holey HEO (0.7Ni)		 **58** 18 23	14	48
Blank		\	24	\

[a] Reaction conditions: 15 ml of substrate, 10 mg of catalysts, O_2 1 atm, 120 °C.

Comparative tests of lacking arbitrary one component in the material synthesis process were performed and the corresponding catalytic performances were shown in Table S4. It can be observed that the quaternate catalysts only show a conversion of about 20% after 24 hours of catalytic reaction and the lack of arbitrary one element has the similar influence on the catalytic activity. Furthermore, the single component and two, three components catalysts exhibit poorer catalytic performance, and the conversions are as low as the bulk HEO. The above catalytic results indicate that there is no obvious difference in the role of the five metal elements in the catalysis reaction, and each metal element could simultaneously serve as benzyl alcohol adsorbents and active sites, which greatly promotes the improvement of catalytic efficiency and provides potentiality for the ultra-high catalytic activity.

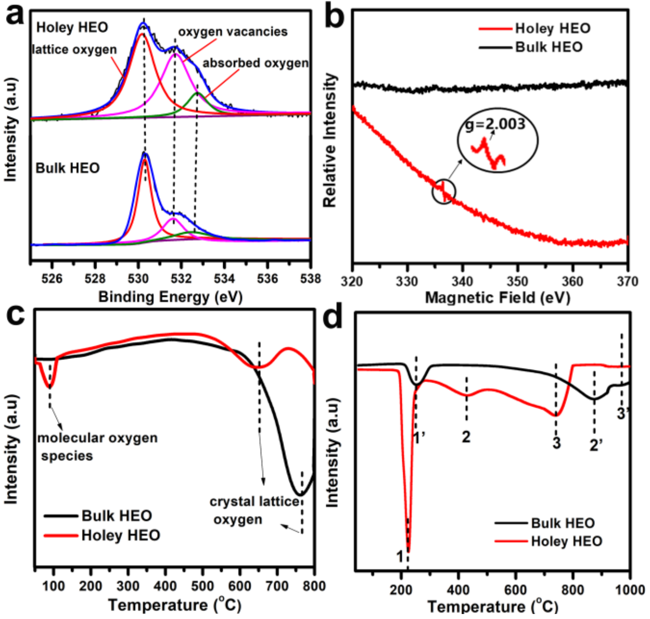


Figure 3. (a) Oxygen XPS spectrum comparison of holey and bulk HEO. (b) EPR spectra of holey and bulk HEO. (c) O_2-TPD and (d) H_2-TPR spectra of holey and bulk HEO.

To better understand the mechanism of the ultra-high catalytic activity, X-ray photoelectron spectroscopy (XPS) spectra of the holey HEO catalyst were recorded, and the bulk HEO was employed as a comparative sample. Figure S8 shows the XPS survey spectra, demonstrating the co-existing of Co 2p, Ni 2p, Cu 2p, Mg 2p, Zn 2p, and O 1s in both bulk and holey HEO. As shown in Figure 3a, the O 1s spectrum of holey lamellar HEO can be fitted into three distinct peaks. The main peak located at 530.7 eV can be ascribed to oxygen ions in the crystal lattice, peak at about 531.6 eV is attributed to oxygen vacancies and peak at 532.9 eV corresponds to surface labile oxygen.[34,35] Among the various oxygen species, the content of oxygen vacancies in holey HEO is up to 39%. The generation of oxygen vacancies is mainly attributed to the following aspects: (i) Oxygen vacancies formed by reducing the HEO particle size to the nanoscale level. It is reported and validated that the energy required for the formation of an oxygen vacancy in small nanoparticles is much lower than for the regular surface, and the oxides with smaller particle size(＞10 nm) tend to generate more oxygen vacancy defects than that of bulk materials. (ii) The random substitutional doping and arrangement of the five metal atoms in HEO structure facilitate the formation of oxygen vacancies. (iii) The grab and consumption of surrounding lattice oxygen atoms from oxides during the rGO combustion process produce an oxygen deficiency atmosphere and results in more oxygen vacancies. However, for bulk HEO, the relative peak strength of defective oxygen is much weaker than that of the holey ones. The difference in O1s spectra indicates that there are abundant oxygen vacancies in holey lamellar HEO. The presence of oxygen vacancies can enhance the dehydrogenation rate of benzyl alcohol substrate, which greatly improved the catalytic activity of the catalyst.[36] The high-resolution XPS spectra of metal elements were shown in Figure S9.

The density of oxygen vacancies of holey HEO can be controlled by adjusting the calcination temperature (Figure S10). As the calcination temperature increases to 1000 °C, the HEO particles show obvious sintering phenomenon, and the content of oxygen vacancies drops by nearly half to 22%. Further increasing the calcination temperature to 1100 °C, the corresponding morphology and oxygen vacancies content are similar to that of the bulk HEO. Both of the above two catalysts exhibit low catalytic activity similar to bulk HEO. The presence of oxygen vacancies can be further evidenced by X-band electron paramagnetic resonance (EPR). As shown in Figure 3b, a weak EPR signal of holey lamellar HEO at g=2.003 can be observed, which is characteristic of single-electron trapped oxygen vacancies.[37]

The O_2-TPD experiment was carried out to investigate the oxygen species over the holey lamellar HEO. As shown in Figure 3c, the desorption peaks located at about 100 °C, 150-500 °C and 600-800 °C are attributed to molecular oxygen species adsorbed on oxygen vacancies, surface labile oxygen and crystal lattice oxygen, respectively. Compared with bulk HEO, the holey lamellar HEO possesses broader peak at about 100 °C, demonstrating higher oxygen vacancies contents, which agrees with the O 1s XPS result. H_2-TPR test was employed to gain insights into the effect of oxygen vacancies on the reducibility of the oxygen species on holey lamellar HEO. As shown in Figure 3d, compared with bulk HEO, the intensity of hydrogen consumption peaks for the holey lamellar HEO are much stronger and the three peaks dramatically shift to lower temperatures in the reduction process, demonstrating the better oxygen delivery capacity in oxygen vacancy-abundant holey lamellar HEO.[38]

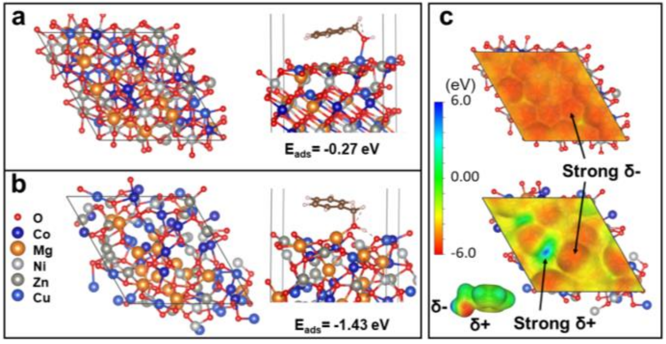


Figure 4. DFT-calculated conformation of adsorption states and adsorption energies of a benzyl alcohol molecule on (a) bulk HEO and (b) holey HEO. (c) Electron localization function maps of bulk HEO (the upper one) and holey HEO (the lower one).

Oxygen vacancies are one of the fundamental and inherent defects of oxide materials, which have an important influence on their catalysis performance. DFT calculations were employed to demonstrate the role of oxygen vacancies in the adsorption process of benzyl alcohol molecules.[39,40] Due to the five elements play the same role in the reaction, the values of adsorption energies (E_{ads}) calculated by selecting arbitrary element as adsorption site are close to each other, which is verified by the similar E_{ads} values obtained via randomly selecting Cu and Mg as the adsorption sites in bulk HEO modeling (Figure S11). Figure 4a and 4b reveal that the E_{ads} of holey lamellar HEO is 1.43 eV, five times larger than that of bulk material (0.27 eV), indicating that the benzyl alcohol is more easily adsorbed on holey lamellar catalyst. This result is attributed to the metal catalytic sites near oxygen vacancies possessing stronger adsorption capacity towards the hydroxyl groups in benzyl alcohol. As shown in Figure 4c, for an ideal HEO, the surface electrostatic potential is dominated by oxygen and shows negative potential. For the vacancy-abundant holey lamellar HEO, many metal ions are exposed on the surface of the material, and the electrostatic potential near these metal ions is positive. When the -OH group of benzyl alcohol approaches, the H combines with the surface oxygen by hydrogen bond, and the O combines with the positively charged metals through metal-oxygen bond, greatly increasing the adsorption energy.[41,42] However, for bulk HEO, the OH—O angle is too small to form hydrogen bond (Figure S12). Thus, H in benzyl alcohol molecule cannot form hydrogen bond with surface oxygen on bulk HEO as the case in holey HEO.

To elucidate the contribution of HEO in catalytic reactions, comparative catalytic tests of the quaternary, ternary, binary and single metal oxide catalysts were performed under the premise of not changing the holey lamellar structure (Table S5), and their corresponding oxygen vacancies contents were estimated by O XPS (Figure S13). The XPS results show that the oxygen vacancies contents of above catalysts are 22%, 25%, 41% and 37% respectively, showing an increasing trend with metal element species increases. It's worth noting that oxygen vacancies contents in quaternary and ternary catalysts are similar with holey lamellar HEO but these catalysts exhibit much lower catalytic activity. According to the above, in addition to oxygen vacancies, the HEO material with unique crystal structure is indispensable to its ultra-high catalytic properties.

On the basis of above findings, the ultra-high catalysis performances of holey lamellar HEO are mainly attributed to the following aspects: (i) The unique structure of elements randomly distributed on the atomic scale endows the HEO material unexpected catalytic properties for the oxidation of benzyl alcohol. (ii) When the high-entropy oxide particles get as small as nanoscale, a large number of oxygen vacancies appear among the material. The presence of oxygen vacancies boosts the oxygen delivery capacity and greatly improves the adsorption energy towards benzyl alcohol, making the oxidation reaction more easily be triggered. (iii) The interconnected HEO nanoparticles prepared by the anchoring-merging process form the holey lamellar framework, and the unique holey lamellar structure provides high specific surface areas and abundant exposed catalytic active sites for the catalytic reaction, leading to exponentially increased oxidation efficiency. Consequently, the synergistic effect of the unique HEO material, abundant oxygen vacancies and holey lamellar framework together leads to the ultra-high catalytic activity.

Conclusion

In conclusion, we have demonstrated that the holey lamellar HEO ($Co_{0.2}Ni_{0.2}Cu_{0.2}Mg_{0.2}Zn_{0.2}O$) catalyst prepared by a simple anchoring-merging process was ultra-highly efficient for the solvent-free aerobic atmospheric oxidation of benzyl alcohol. The presence of abundant oxygen vacancies and exposed catalytic sites in the catalyst significantly enhances their catalytic efficiency, and up to 98% conversion rate can be achieved at 120 °C in only 2 hours. By rational regulating the catalytic reaction parameters, we can selectively optimize benzoic acid or benzaldehyde as the dominant product. This study is significant in the utilization of HEO material with unique architecture and indeed give a brilliant perspective in the development of heterogeneous catalysts in industrial catalysis area.

Acknowledgements

This work was supported by the Young Thousand Talented Program and the National Natural Science Foundation of China (21671073 and 21621001), the “111” Project of the Ministry of Education of China (B17020), Program for JLU Science and Technology Innovative Research Team. SD was supported by U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

Keywords: porous material• anchoring and merging process • mesoporous structure • high entropy oxide • oxidation of benzyl alcohol

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10.1002/ange.202004892

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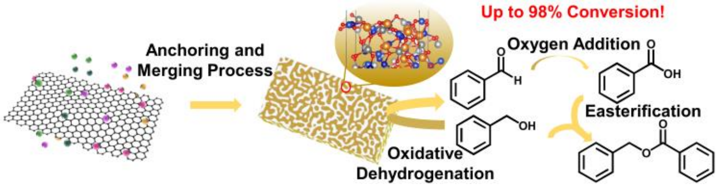

A novel high entropy oxide material with mesoporous structure is prepared by an anchoring and merging process, and exhibits ultra-high catalytic activity for the oxidation of benzyl alcohol. Benzoic acid or benzaldehyde can be selectively optimized as the main product by rational regulating the catalysis parameters. The ultra-high catalysis performance is attributed to the synergistic effect of the porous framework and abundant oxygen vacancies.

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Holey Lamellar High Entropy Oxide as Ultra-Highly Active Heterogeneous Catalyst for Solvent-free Aerobic Oxidation of Benzyl Alcohol