Novel cerium oxide-type high entropy rare earth oxides for photocatalytic CO_2 hydrogenation

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Introduction

Photocatalytic CO2 conversion is a promising clean technology for reducing greenhouse gases in the atmosphere. A semiconductor photocatalyst absorbs light and converts CO2 via various pathways, resulting in different products. However, for photocatalytic CO2 conversion to be possible, the photocatalyst must possess specific qualities, such as appropriate bandgap, band structure, etc. Even though there are many photocatalysts available nowadays, it is crucial to continue searching for new and highly active photocatalyst materials to achieve practical applications. The study of high entropy oxides (HEOs) has emerged as a rapidly growing and dynamic field within material science. These materials, consisting of a mixture of various elements in single-phase compounds, are known for their unique properties and crystal structures due to their high configurational entropy. In this research, six ceria-based high entropy oxides were prepared using an environmentally friendly sol–gel citrate route. To better understand the photocatalytic behavior, we conducted thorough structural analysis and surface studies. The catalytic performance of the oxides was investigated via a model heterogeneous reaction (photocatalytic CO2 hydrogenation), by which we proved their possible application as highly efficient photocatalysts for CO2 conversion.

Conclusions

In terms of photocatalytic activity, the results show that O2 has the highest CO_2 conversion efficiency, which is 4.47 times higher than that of pure CeO_2. O1 has a moderate photocatalytic activity with a 1.12 times improvement compared to pure CeO_2, while O5 and O6 have slightly lower photocatalytic activity than O2. The results have shown that the catalytic properties of high entropy oxides can be tuned by selecting the appropriate constituents. Specifically, we found that ceria-based high entropy oxides have great potential as photocatalysts for CO_2 hydrogenation reaction when tuned correctly. Our research provides a foundation for further exploration of high entropy oxides as potential photocatalysts for CO_2 hydrogenation, which could have significant implications for addressing climate change. We hope that our findings will motivate further investigation and development of high entropy oxides for this application and that this research will help to place high entropy oxides at the forefront of emerging materials for photocatalytic reactions.

Results

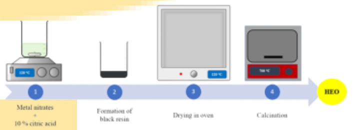

Figure 1. Schematic representation of the modified citrate route.

Table 1. List of synthesized high entropy compounds.

Compound	Chemical formula
O1	$Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Y_{0.2}O_2$
O2	$Ce_{0.2}Zr_{0.2}La_{0.2}Nd_{0.2}Sm_{0.2}O_2$
O3	$Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Nd_{0.2}O_2$
O4	$Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Sm_{0.2}O_2$
O5	$Ce_{0.2}Zr_{0.2}La_{0.2}Nd_{0.2}Y_{0.2}O_2$
O6	$Ce_{0.2}Zr_{0.2}La_{0.2}Sm_{0.2}Y_{0.2}O_2$

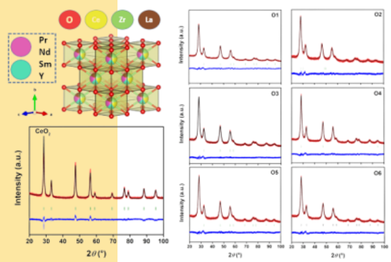

Figure 2. Rietveld plot of the synthesized HEO catalysts with visualized fluorite-type crystal structure.

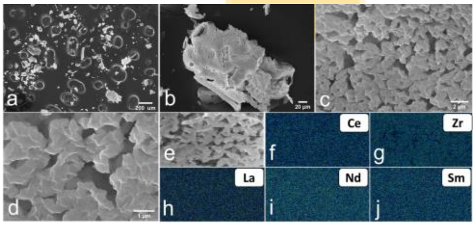

Figure 3. (a–d) Low and high magnification SEM images of O2 catalyst; (e) High magnification SEM image used for EDS mapping; (f–j) Elemental maps of O2 catalyst showing the uniform distribution of cations.

Table 2. Photocatalytic CO2 hydrogenation and characterization results of the investigated ceria-based high entropy oxides.

Compound	S_{BET} [m^2g^{-1}]	Pore size [nm]	Total pore volume [cm^3g^{-1}]	Band gap [eV]	Average crystallite size [nm]	Conversion [%]	Formation rate [nmol g^{-1} sec^{-1}] CO	Formation rate CH_4	Formation rate CH_3OH	Selectivity [%] CO	Selectivity CH_4	Selectivity CH_3OH
CeO_2	21.5	12.1	0.065	3.74	11	6.6	308.1	0	0	100	0	0
O1	24.9	10.7	0.067	2.73	4	7.4	332.2	18.7	0	94.6	5.4	0
O2	33.2	14	0.116	3.32	4	29.7	1256.5	4.1	110.3	91.6	0.3	8.1
O3	27.3	13.2	0.09	2.65	4	7.9	364.5	8.2	1.3	97.4	2.2	0.4
O4	24.2	12.9	0.078	2.93	5	9.2	393.1	37.8	2.9	90.6	8.8	0.6
O5	35.7	13.6	0.121	3.37	4	19.3	745.1	84.5	77.5	82.1	9.3	8.6
O6	32	13.9	0.111	3.21	4	20.3	763.3	97.1	91.5	80.2	10.2	9.6

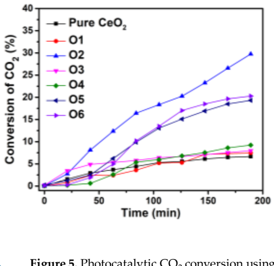

Figure 5. Photocatalytic CO_2 conversion using synthesized high entropy oxides as catalysts, and CeO_2 as parent oxide.

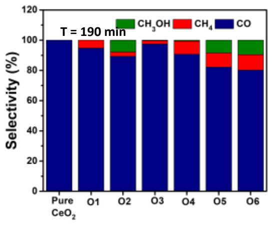

Figure 6. Selectivity of high entropy oxides towards reaction products.

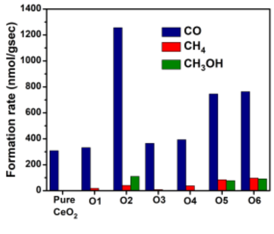

Figure 7. Formation rate of the products using high entropy oxides as photocatalysts.

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