

Enhancing Catalytic Efficiency of High-Entropy Rare-Earth Zirconates Towards Conversion of Greenhouse Gases



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INTRODUCTION

Ceria-zirconia ($\text{CeO}_2\text{-ZrO}_2$) system has attracted attention in the last decade due to its outstanding catalytic activity and stability. Since nanocrystalline ceria-zirconia-based compounds exhibit oxygen-rich surfaces that can be used in oxidation reactions, they are often used in the methane oxidation process. Introducing high-entropy by adding rare-earth elements in ordered ceria-zirconia systems gives whole new promising class of multifunctional materials characterized by their ability to stabilize complex and having enhanced catalytic activity due to oxygen vacancies and lattice distortions, especially towards CO_2 reduction reactions. Photocatalytic experiments showed that high-entropy pyrochlore phase ($\text{La}_{0.2}\text{Ce}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2}\text{Zr}_2\text{O}_7$) achieves the highest CO_2 conversion rate under visible-light irradiation remarkably surpassing pure ceria and zirconia. Temperature-programmed desorption was conducted in CH_4/Ar atmosphere and showed that high-entropy forms of starting oxide $\text{La}_{0.1}\text{Ce}_{0.1}\text{Pr}_{0.1}\text{Gd}_{0.1}\text{Y}_{0.1}\text{Zr}_{0.5}\text{O}_2$ and its re-oxidized counterpart ($\text{La}_{0.2}\text{Ce}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2}\text{Zr}_2\text{O}_8$) have the largest amount of ion current change, i.e. the production of carbon dioxide is larger than with other forms of oxides due to greater oxygen storage capacity (OSC). Obtained compounds were also subjected to in detail structural, microstructural and spectroscopic analysis to determine the improvement of physicochemical properties.

RESULTS

Table 1. List of prepared compound acronyms along with their chemical formula.

Synthesized compound	Chemical formula
CeZrO	$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$
p-CeZrO	$\text{Ce}_2\text{Zr}_2\text{O}_7$
k-CeZrO	$\text{Ce}_2\text{Zr}_2\text{O}_8$
LCPGY	$\text{La}_{0.1}\text{Ce}_{0.1}\text{Pr}_{0.1}\text{Gd}_{0.1}\text{Y}_{0.1}\text{Zr}_{0.5}\text{O}_2$
p-LCPGY	$(\text{La}_{0.2}\text{Ce}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_7$
k-LCPGY	$(\text{La}_{0.2}\text{Ce}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Y}_{0.2})_2\text{Zr}_2\text{O}_8$

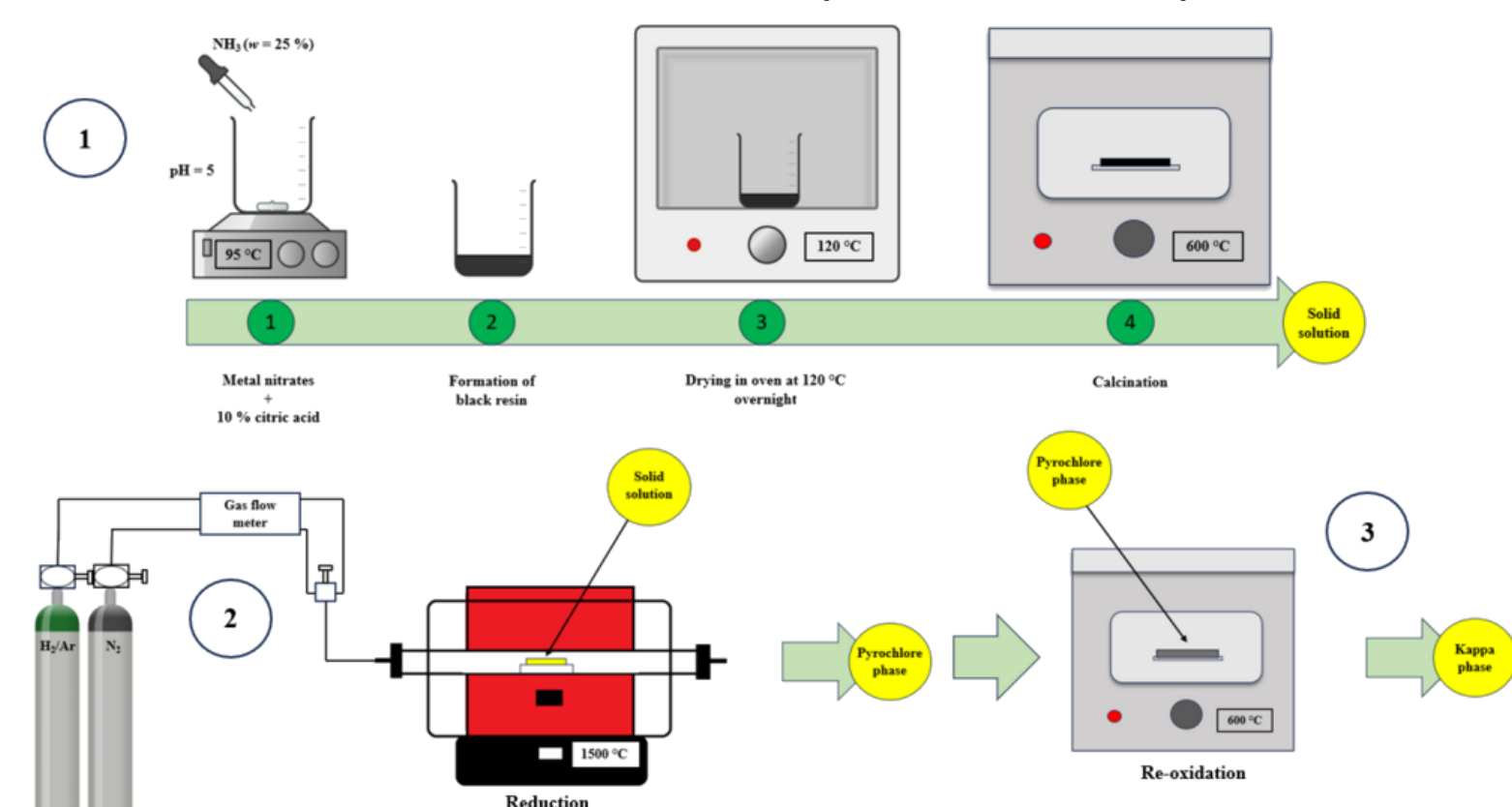


Figure 1. Schematic overview of the synthesis path.

Table 2. Overview of the results of photocatalytic CO_2 hydrogenation.

Compound	Conversion (%)	Selectivity (%)	Space Time Yield ($\text{mmol g}^{-1}\text{h}^{-1}$)
CeO_2	6,05	100	24.34
ZrO_2	7,33	100	29.48
CeZrO	9,78	100	30.98
p-CeZrO	15,03	100	66.23
k-CeZrO	20,74	100	83.36
LCPGY	11,99	100	47.2
p-LCPGY	24,14	90	87.14
k-LCPGY	21,76	94,8	5,2

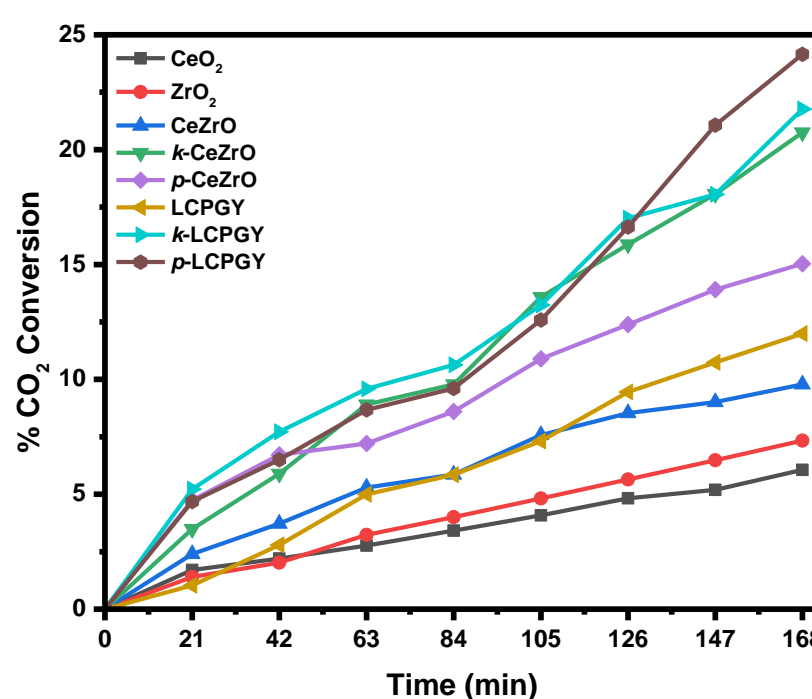


Figure 2. Photocatalytic conversion of CO_2 under visible light.

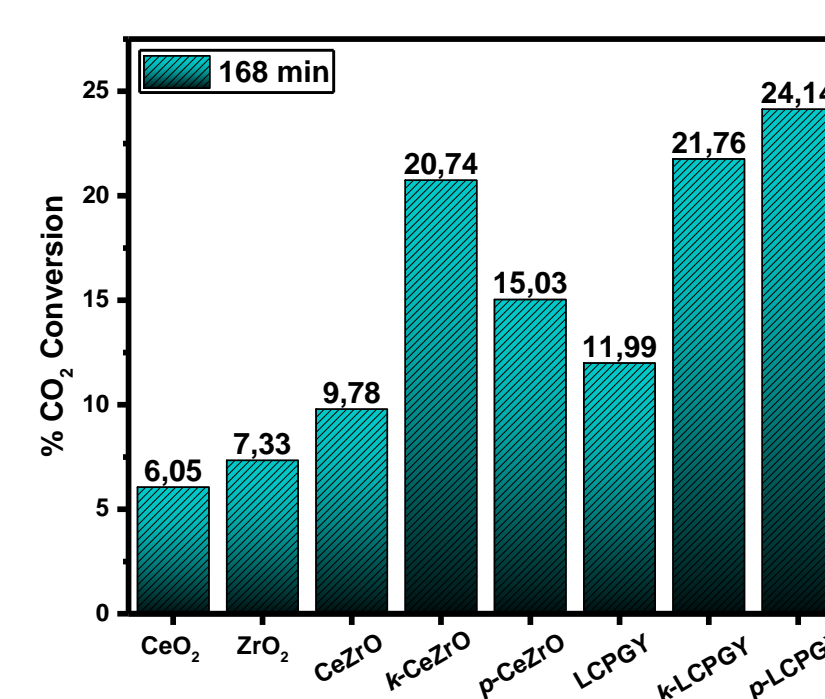


Figure 3. Selectivity of the catalysts towards reaction products.

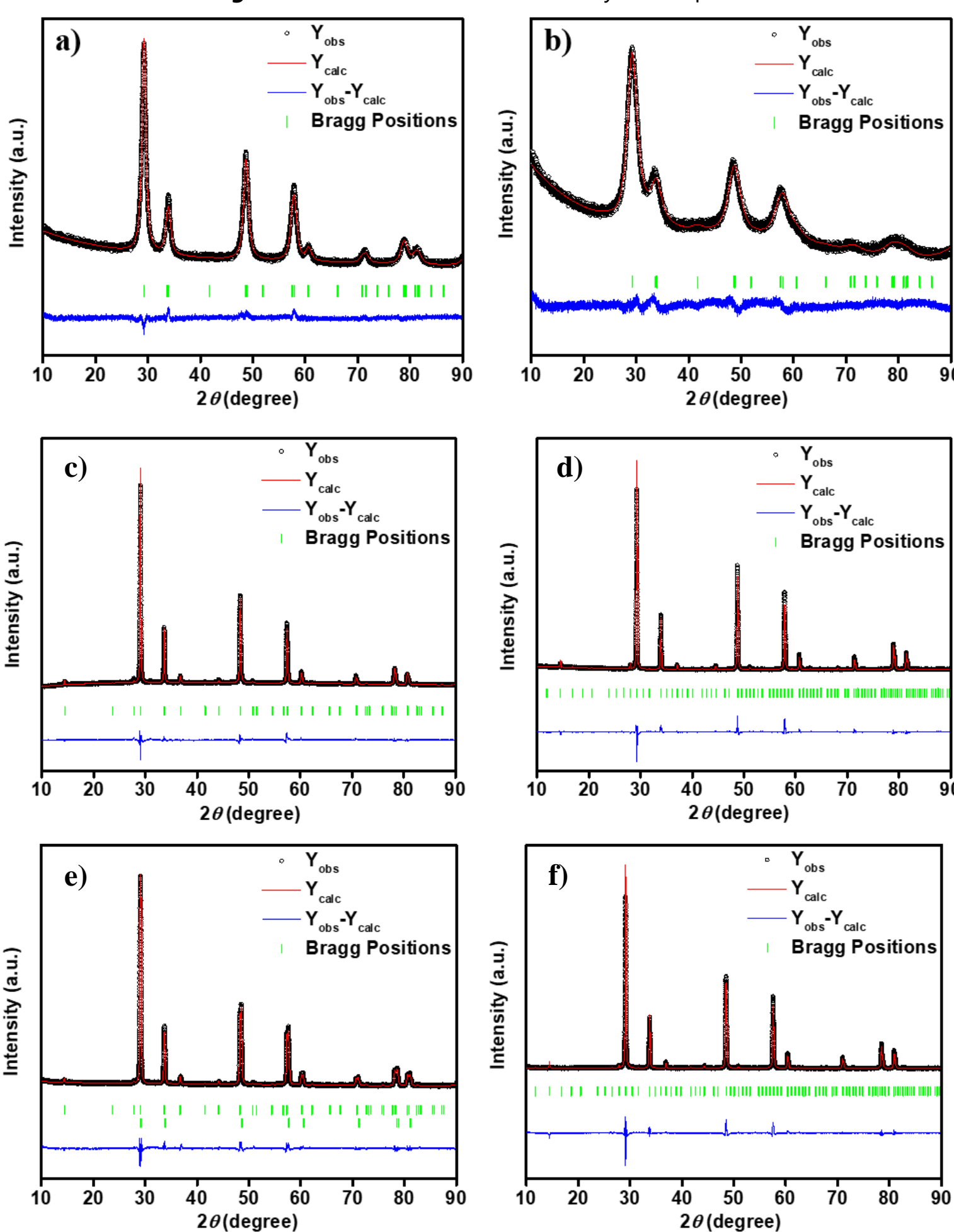
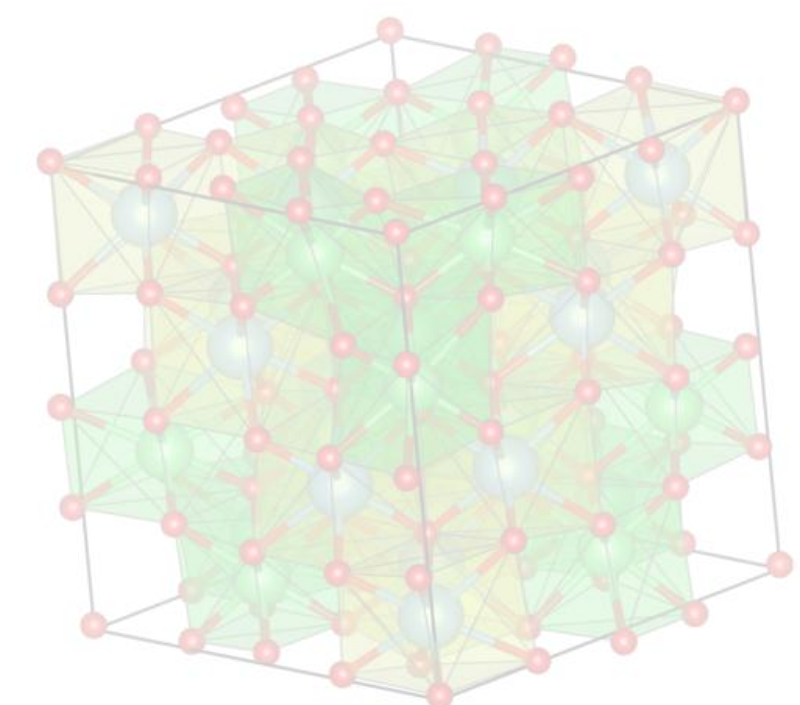


Figure 4. Rietveld plots of (a) CeZrO, (b) LCPGY, (c) p-CeZrO, (d) k-CeZrO, (e) p-LCPGY, (f) k-LCPGY.

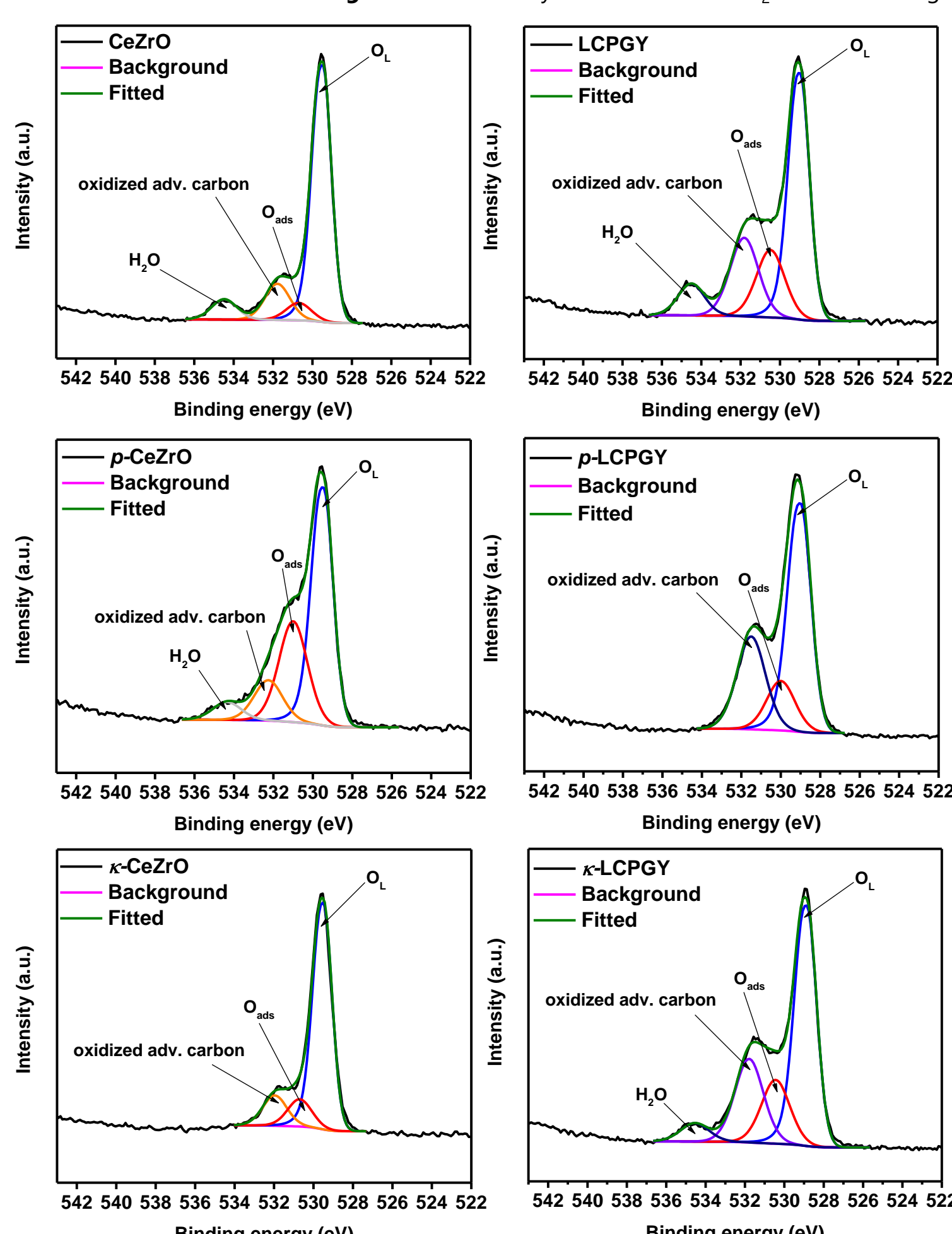


Figure 5. Deconvoluted O 1s XPS spectra of synthesized catalysts.

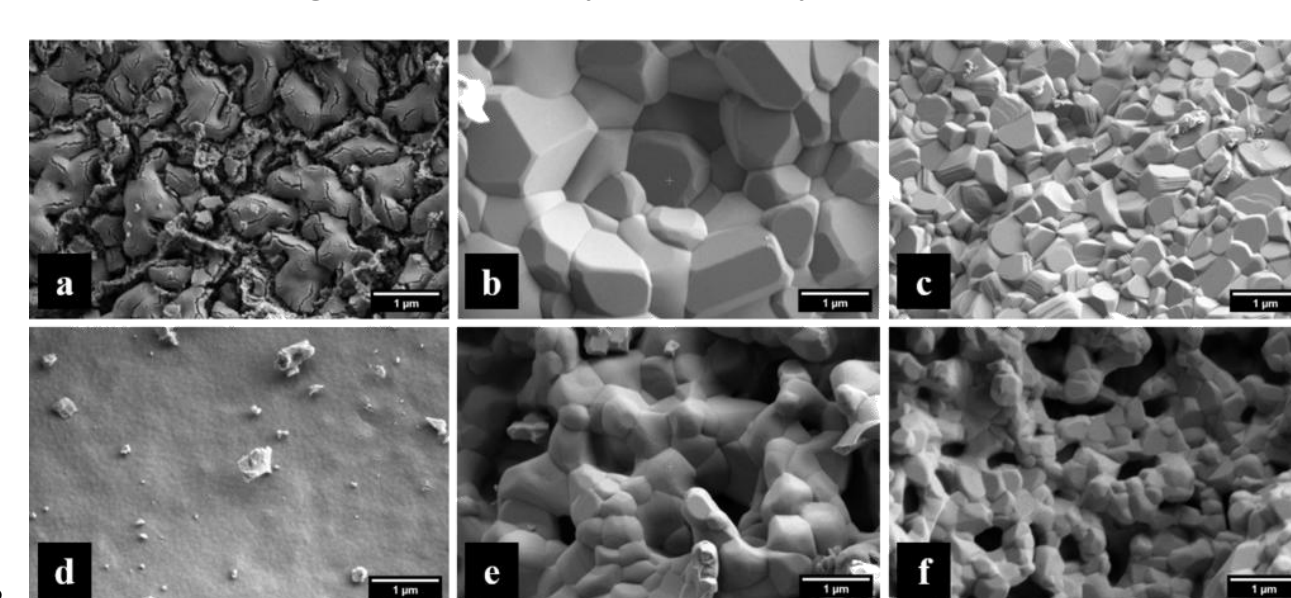


Figure 6. SEM images of (a) CeZrO, (b) p-CeZrO, (c) k-CeZrO, (d) LCPGY, (e) p-LCPGY, (f) k-LCPGY.

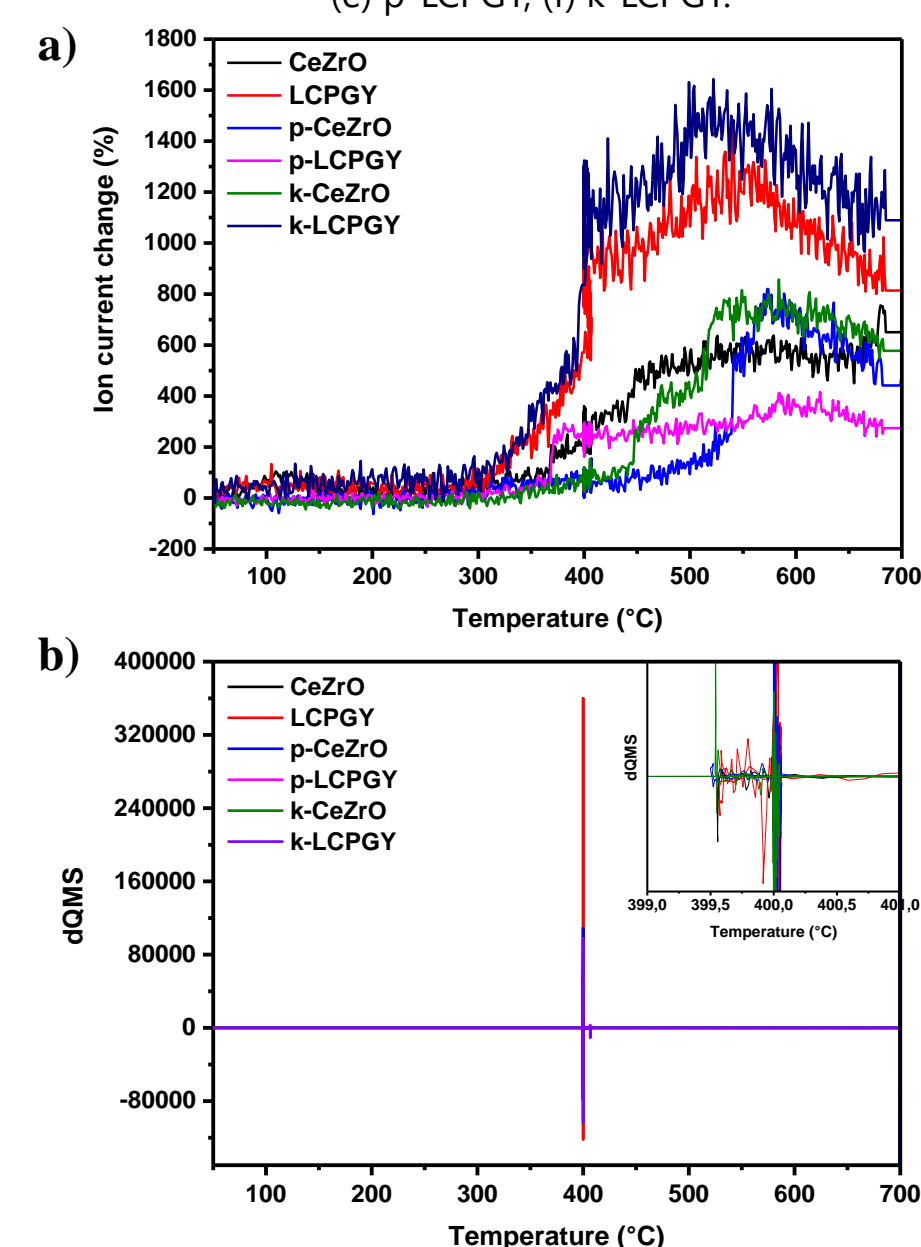


Figure 7. a) Ion current change and b) Differential ion current change as a function of temperature during the exposure of synthesized compounds to methane flow (100 mL/min).

CONCLUSIONS

This research highlights the impact of introducing high entropy using rare-earth elements in the $\text{CeO}_2\text{-ZrO}_2$ system. The crystallographic analysis demonstrates that both pyrochlore (*p*-) and kappa (*k*-) phases have been successfully formed in this system using modified sol-gel synthesis and oxidation-reduction reactions. Rietveld plot of high-entropy rare-earth zirconate pyrochlore phase, *p*-LCPGY, showed that it exhibits pyrochlore-fluorite dual-phase which is controlled by the size disorder (δ^*), average cation radius ratio (r_A/r_B) and the configuration entropy (S_{conf}). Applying high-entropy into the ceria-zirconia system turned out as a promising way of obtaining photocatalysts for CO_2 hydrogenation under visible light. The findings prove the role of high configurational entropy, multi-element synergy, and defect engineering in enhancing catalytic performance. Between all the catalysts, *p*-LCPGY showed the highest photocatalytic efficiency, achieving a CO_2 conversion rate of 24.14% and selectivity to both CO (90%) and HCHO (10%). These results can be coupled with optimized charge carrier dynamics facilitated by $\text{Pr}^{3+/4+}$ and $\text{Ce}^{3+/4+}$ redox pairs and abundant oxygen vacancies, which improve charge separation and suppress electron-hole recombination. Temperature-programmed desorption of carbon dioxide (methane oxidation) showed that high-entropy forms of starting oxide and its re-oxidized counterpart have the largest amount of ion current change (Figure 7.). This means that they produce larger amounts of carbon dioxide than other forms of oxides probably because of the larger amount of oxygen at the surface i.e. larger oxygen storage capacity (OSC) since the experiment was conducted in CH_4/Ar atmosphere.