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Sol-gel Synthesis of Ceria-zirconia-based High-entropy Oxides as High-promotion Catalysts for the Synthesis of 1,2-diketones from Aldehyde

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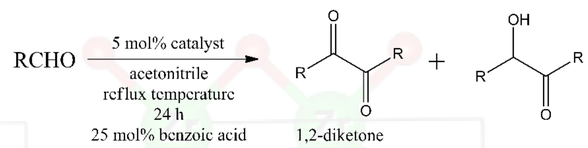
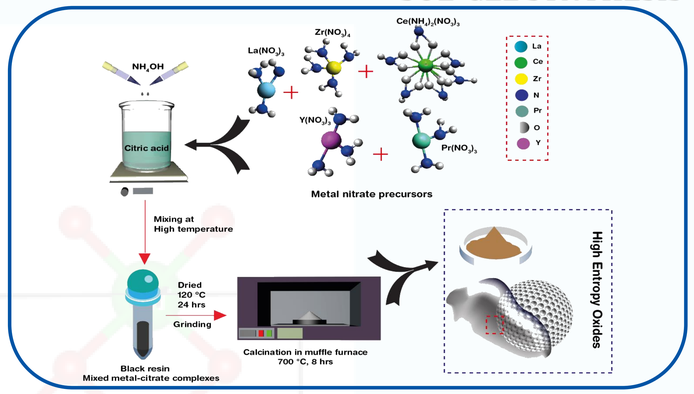
INTRODUCTION

Efficient Lewis-acid-catalyzed direct conversion of aldehydes to 1,2-diketones in the liquid phase was enabled by using newly designed and developed ceria–zirconia-based high-entropy oxides (HEOs) as the actual catalysts. The synergistic effect of various cations incorporated in the same oxide structure (framework) was partially responsible for the efficiency of multicationic materials compared to the corresponding single-cation oxide forms. Furthermore, a clear, linear relationship between the Lewis acidity and the catalytic activity of the HEOs was observed. Due to the developed strategy, exclusively diketone-selective, recyclable, versatile heterogeneous catalytic transformation of aldehydes can be realized under mild reaction conditions. Studied HEOs exhibit bandgaps in the range from 1.91 eV to 3.0 eV and appropriate valence and conduction bands for water splitting. They reveal high photocatalytic activity that is mostly attributed to the accessibility of more photocatalytic active sites which provided radicals responsible for the AZO dye degradation. The materials successfully produce hydrogen by photocatalytic water splitting, suggesting the potential of HEOs as new photocatalysts. The photocatalytic performances of all studied HEOs outperform the single fluorite oxides or equivalent mixed oxides. The $Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Y_{0.2}O_2$ (CZLPY) engender hydrogen in 9.2 μmolmg^{-1} per hour that is much higher content than for pristine CeO_2 material which amounts to 0.8 μmolmg^{-1} per hour.

PINACOL-TYPE OXIDATIVE COUPLING REACTION OF THE ALDEHYDES

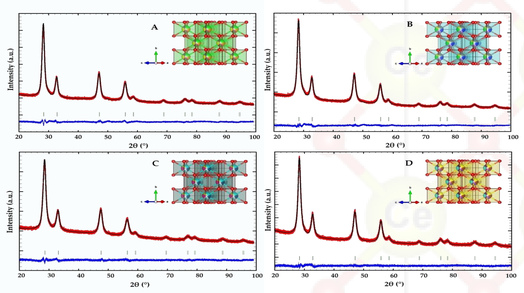


SOL-GEL SYNTHESIS

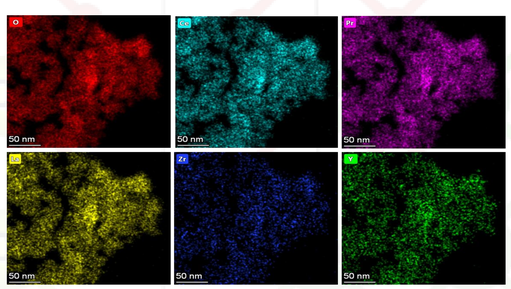


CHARACTERIZATION AND CATALYTIC ACTIVITY FOR ORGANIC SYNTHESIS, AZO DYE DEGRADATION AND HYDROGEN EVOLUTION REACTION

Compound	Chemical formula	Pore volume (cm^3/g)	S_{BET} (m^2/g)	Average crystallite size (nm)/XRD	Acidity (a.u./g)
CZLEY	$Ce_{0.2}Zr_{0.2}La_{0.2}Eu_{0.2}Y_{0.2}O_2$	0.14	48	6	31
CZLPY	$Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Y_{0.2}O_2$	0.27	103	6	77
CZEYG	$Ce_{0.2}Zr_{0.2}Eu_{0.2}Y_{0.2}Gd_{0.2}O_2$	0.08	51	5	54
CZLPG	$Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Gd_{0.2}O_2$	0.33	60	6	44



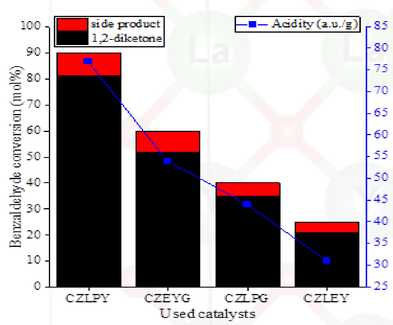
Rietveld plot of the investigated compounds: **(A)** CZLEY; **(B)** CZLPY; **(C)** CZEYG; **(D)** CZLPG. Along with Bragg reflections, the observed (red), calculated (black), and difference (blue) plots are shown for the fit of the PXRD pattern. In the insets of each figure, the fluorite-type crystal structure of the corresponding HEO is visualized.



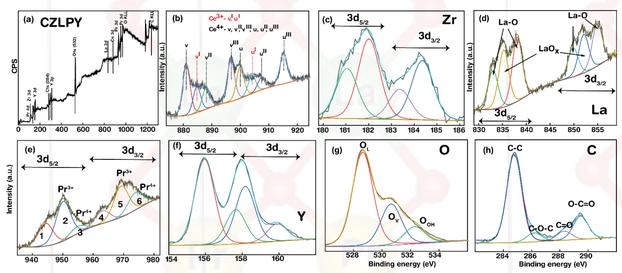
Qualitative EDX maps reveal the uniform distribution of the involved elements inside the powder sample.

Aldehydes	Products	Aldehyde conversion (mol%)	Product yield (mol%)
Acetaldehyde	Diacetyl	80	70
Propionaldehyde	3,4-Hexanedione	76	68
Butyraldehyde	4,5-octanedione	71	61
Benzaldehyde	Benzil	90	81
Furfural	Furil	73	66
Vanilin	1,2-Bis-Benzo(1,3)diioxol-5-yl-ethane-1,2-dione	67	60

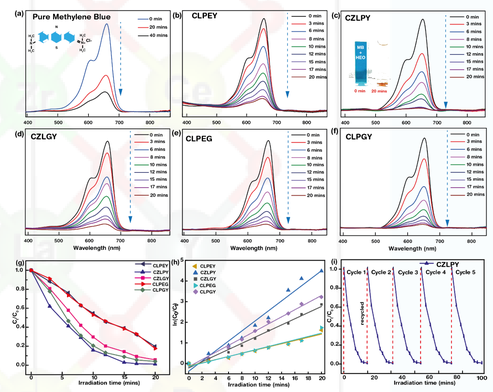
Pinacol-type oxidative coupling reactions of the different aldehydes promoted by the CZLPY catalyst. 1 mmol aldehyde, 2 cm^3 acetonitrile, 0.25 mmol benzoic acid, 5 mol% catalyst, reflux temperature, 24 h.



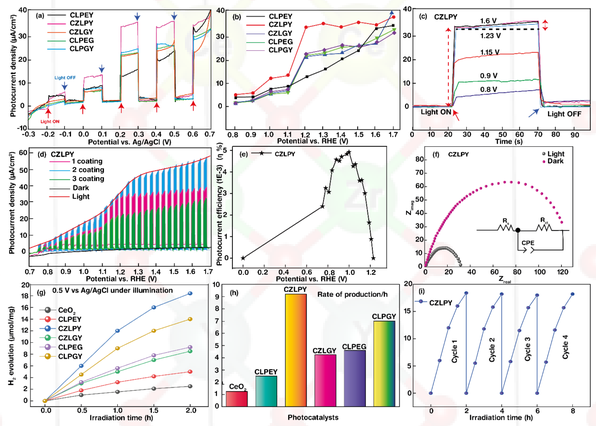
Comparative study of the catalytic ability of the different HEOs to promote the oxidative pinacol-type coupling reaction of the benzaldehyde.



Survey XPS spectrum of CZLPY (a) and high resolution deconvoluted spectra of: (b) cerium, (c) zirconium, (d) lanthanum, (e) praseodymium, (f) yttrium, (g) oxygen and (h) carbon.



UV-Vis absorption spectra of methylene blue (MB) dye under solar illumination (a) without and (b-f) with addition of HEOs monitored at regular interval of time. Inset showing colour degradation of MB dye to colourless solution after treatment with CZLPY and solar irradiation for 20 min; (g) The rate of photocatalytic degradation (C_t/C_0) of MB by HEOs under solar irradiation; (h) Plot of ln (C_0/C_t) vs irradiation time; (i) Re-cyclability test of CZLPY towards MB dye degradation



Photoelectrochemical (PEC) performance of CLPEY, CZLPY, CZLGY, CLPEG, and CLPGY showing LSV plots under chopped dark and solar-light condition. (a) Potential vs. Ag/AgCl (V) and (b) Potential vs. RHE (V); (c) Photo switching transient behaviour of CZLPY electrode at 0.8, 0.9, 1.15, 1.23 and 1.6 V vs. RHE (0.3 V vs. Ag/AgCl = 1.26 V vs. RHE); (d) LSV plots of CZLPY electrode with varied coating thickness (1,2,3) under chopped light and dark conditions (Potential vs. RHE); (e) Applied bias photon-to-current efficiency (ABPE, η%) vs potential in RHE scale plot for CZLPY electrode; (f) Electrochemical impedance spectroscopy data obtained for CZLPY electrode under dark and light condition; (g) Time-dependent hydrogen (H_2) evolution by pure CeO_2, CLPEY, CZLPY, CZLGY, CLPEG, and CLPGY under solar irradiation and their (h) corresponding hydrogen production rate after 2 hours of constant irradiation; (i) Stability test showing catalytic activity of CZLPY catalyst over four sequential cycles.

Saturated photocurrent density and HER activity trend w.r.t. structural properties of the catalysts.

Catalyst	Surface $[O_V+O_H]/[O_V+O_H+O_L]$ (%)	HER activity in 2 hrs (μmolmg^{-1})	Surface $[Pr^{3+}]/[Pr^{3+}+Pr^{4+}]$ (%)	Surface $[Ce^{3+}]/[Ce^{3+}+Ce^{4+}]$ (%)	D_{av} (nm)	ε_{av} (×10^{-4})	S_{BET} (m^{2}g^{-1})	Saturated Photocurrent Density (j) (μAcm^{-2})
CLPEY	24.8	5	76.3	11.9	6	57.50	23.4	17
CZLGY	26.2	8.5	0	14.9	6	38.60	61.4	21
CLPEG	26.6	9.2	77.3	20.4	8	51.73	30.8	22
CLPGY	29.1	14	76.3	22.2	7	58.40	23.4	25
CZLPY	40.4	18.4	84.7	19.3	6	25.20	24.3	35

CONCLUSIONS

Ceria–zirconia-based high-entropy catalysts were successfully synthesized. The applied synthetic route, the modified sol-gel citrate route, resulted in phase-pure compounds with a cubic structure, with lattice parameters that differ from pure CeO_2. This is related to the lattice expansion/contraction due to the incorporation of five cations into a single-cation lattice. The investigation of the physicochemical properties of the newly developed and synthesized catalysts shows that the crystallite size, lattice parameters, surface areas, and pore volumes are similar, while the Lewis acidity differs significantly. The pinacol-type oxidative coupling reaction of the aldehydes was presented, using HEOs as the actual catalysts, which demonstrated the catalytic abilities and chemoselectivity of the catalysts. Upon using the HEOs as the catalysts, the desired diketone product was produced with almost the same selectivity, unlike the activity, which followed the trend of increasing acidity. CZLPY oxide proved to be a versatile, reusable, and heterogeneous catalyst.

Among studied HEOs, $Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Y_{0.2}O_2$ (CZLPY) has shown the highest photocatalytic activity in AZO dyes degradation and photocatalytic water splitting in hydrogen generation than any other synthesized HEOs due to the presence of optimum level of Pr^{3+}, Ce^{3+} and the highest content of oxygen vacancies as verified by XPS. Thus, the phase stabilization of high-entropy oxide in parent CeO_2 lattice induced more lattice distortion, more Ce^{3+} concentration, more oxygen vacancies and additional energy levels (due to more oxidation states of Ce and Pr) as compared to pure CeO_2.