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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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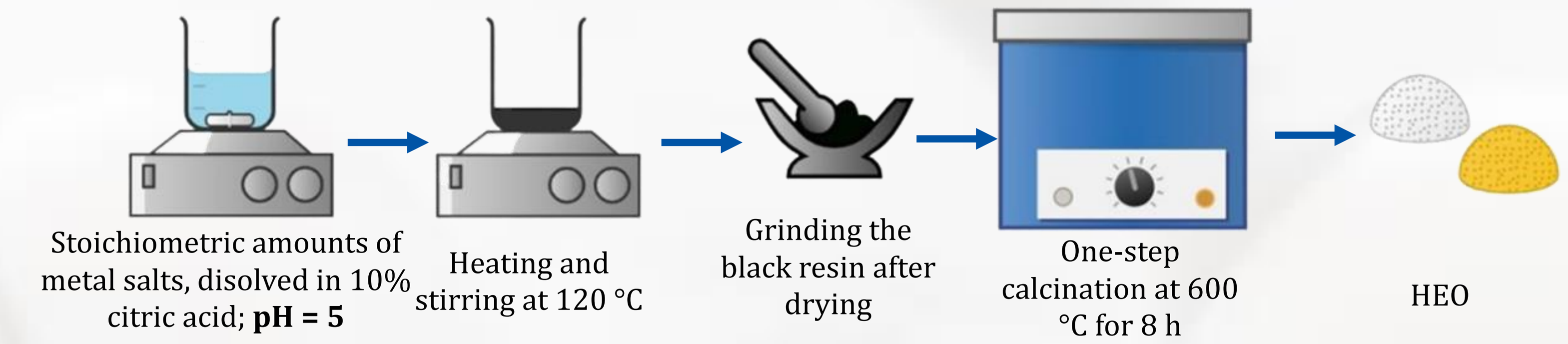
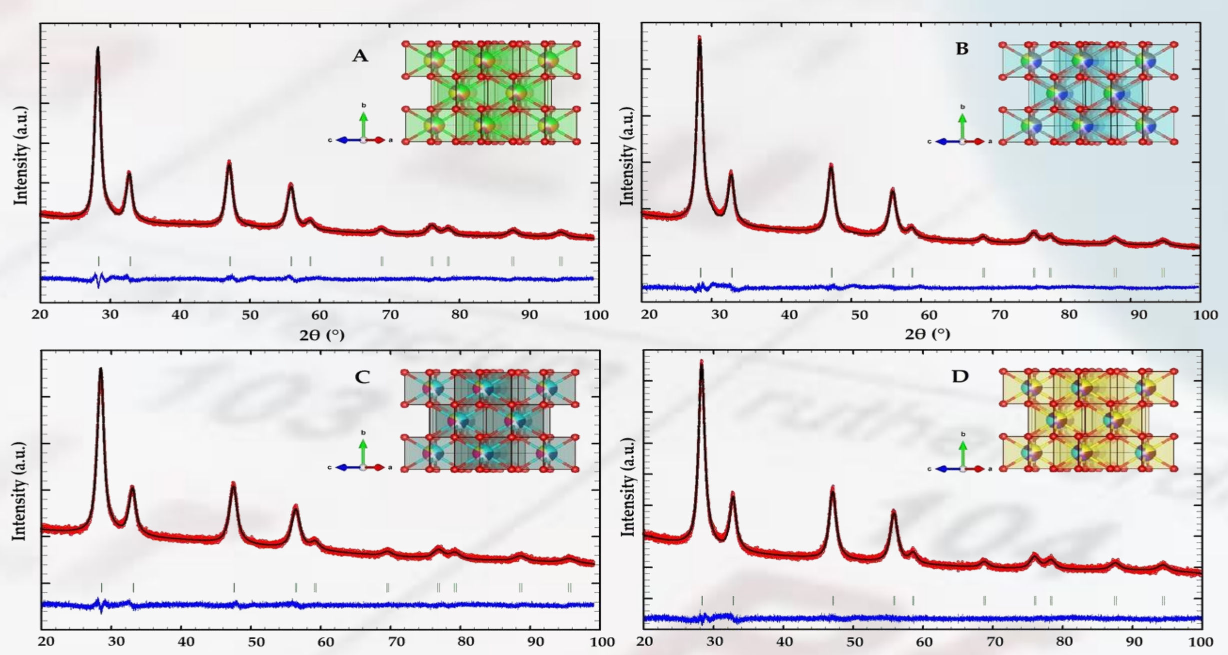
INTRODUCTION

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 (frameworka) 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.

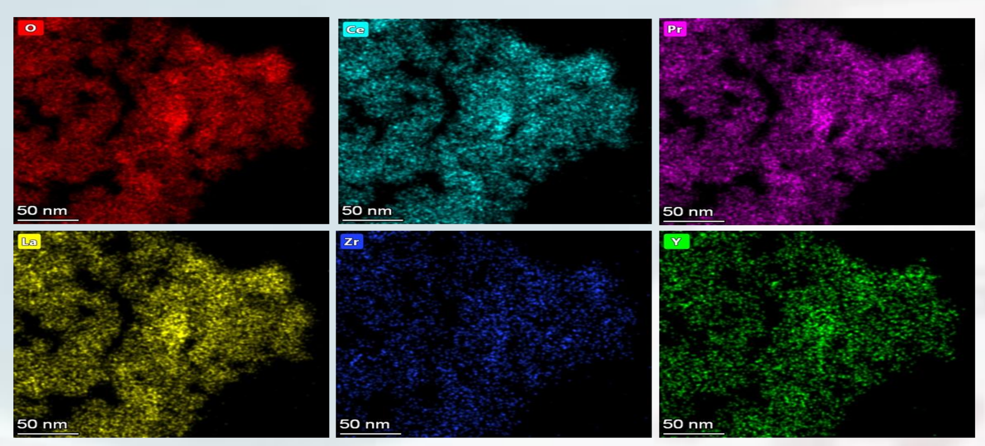
SOL-GEL SYNTHESIS



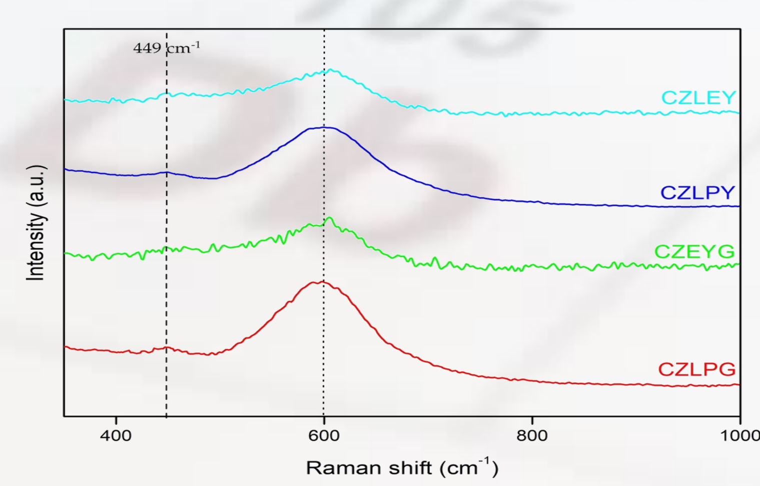
STRUCTURAL CHARACTERIZATION



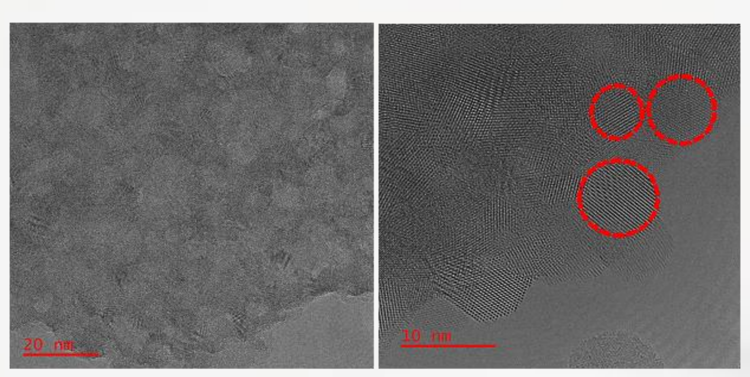
Rietveld plot of the investigated compounds: **(A)** CZLEY; **(B)** CZLPY; **(C)** CZEYG; **(D)** CZLPG. Along with Bragg reflections, the observed (red), calculated (black), and difference (blue) plots are shown for the fit of the PXRD pattern. In the insets of each figure, the fluorite-type crystal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



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



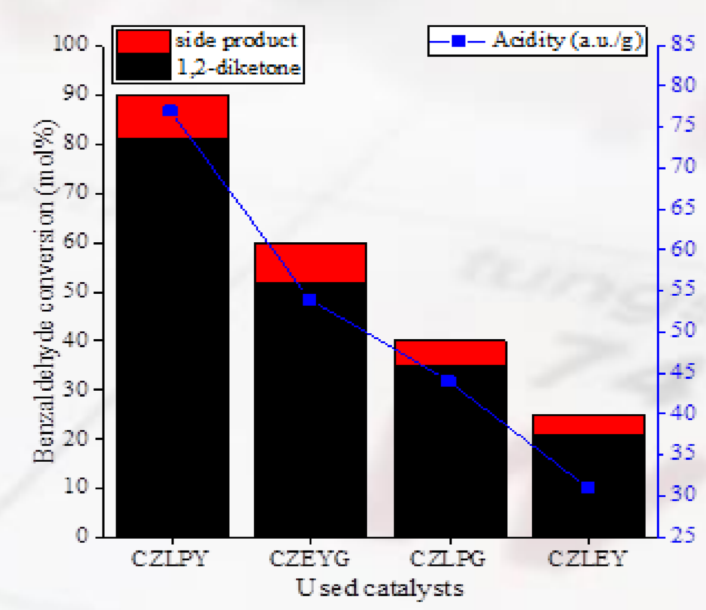
Raman spectra of the synthesized HEOs. F_{2g} band shift of ~15 cm^{-1} is related to the expansion of the crystal lattice, the bond lenghts, and the formation of oxygen defects. Additional bands at ~600 cm^{-1} are related to oxygen defects.



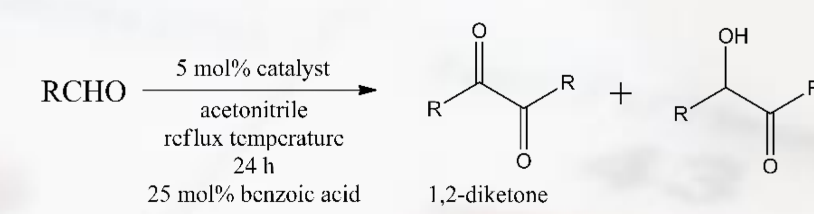
TEM/HRTEM images of the CZLPY powder sample at different magnifications confirms that average crystallite size is less than 10 nm

Compound	Chemical formula	Pore volume (cm^3/g)	S_{BET} (m^2/g)	Average crystallite size (nm)/XRD	Average crystallite size (nm)/HRTEM	II_D/II_{F2g}	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	-	1.30	31
CZLPY	$Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Y_{0.2}O_2$	**0.27**	**103**	**6**	**6**	**1.81**	**77**
CZEYG	$Ce_{0.2}Zr_{0.2}Eu_{0.2}Y_{0.2}Gd_{0.2}O_2$	0.08	51	5	-	1.44	54
CZLPG	$Ce_{0.2}Zr_{0.2}La_{0.2}Pr_{0.2}Gd_{0.2}O_2$	0.33	60	6	-	1.90	44

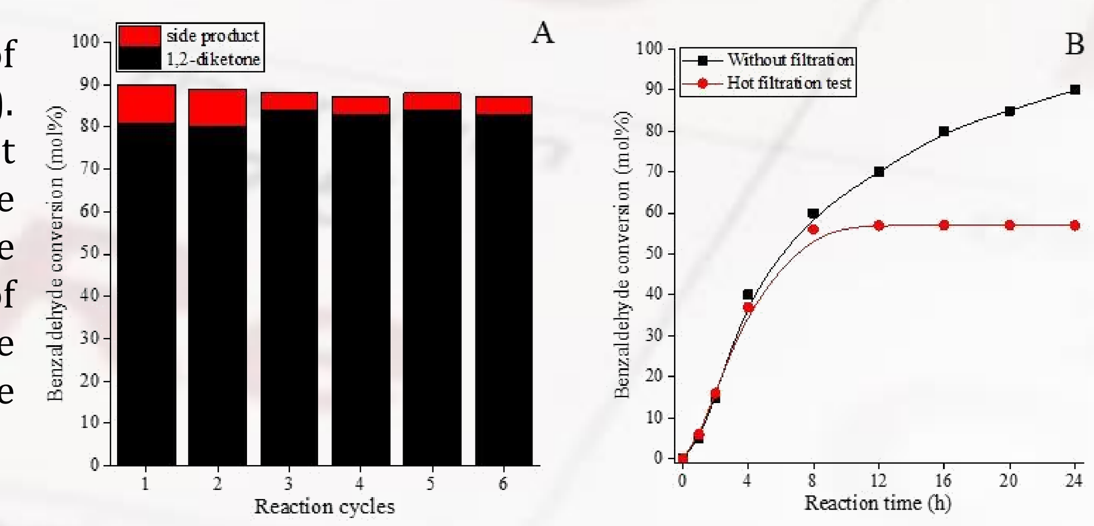
CATALYTIC ACTIVITY



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



Recyclability test of the CZLPY catalyst **(A)**. Heterogeneity (hot filtration) test of the pinacol-type oxidative coupling reaction of the benzaldehyde catalyzed by the CZLPY catalyst **(B)**.



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.

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

CONCLUSIONS

Four 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.