

# Synthesis of 1,2-diketones From Aldehyde Using Novel Ceria-Zirconia High-Entropy Oxides as Actual Catalysts

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## Introduction

One of the main objectives in materials science: finding new, advanced materials, has become a priority. One of the newest class of those materials, that attracted much scientific attention, are high entropy oxides. To obtain a phase pure, single-phase oxide system, several conditions are necessary to meet. General principles, when choosing appropriate constituents, rely on consideration of ionic radii, oxidation state, and coordination number of cations that will occupy a single cation sublattice, while the anion sublattice is only occupied by oxygen. Much attention has been also focused on the synthesis of 1,2 diketones and their derivatives for a long time. In this context, several synthesis strategies have been designed and developed, including such attractive methodologies that realize under catalytic conditions. Although notable progress has been attained with precious noble metal catalysts, more recently, considerable advances have been obtained by using Lewis acids, having more profitable qualities to noble metals. Moreover, these catalysts proved to be well fitted for any other catalytic views as well, such as low toxicity and significant functional group tolerance. However, for performing the well-optimized reaction sequence, which consists of a Sonogashira-type decarboxylative coupling and oxidation, the application of arylboronic acids or aryl iodides with alkynyl carboxylic acids as raw materials is essential, reducing substantially the eco-friendly feature of these systems. There is a less familiar fact that an oxidative Pinacol-type coupling should be also sufficient to produce diketones that can be also promoted by Lewis acids. However, the most effectiveness can be achieved by adding organic additives in these cases. The above trends have motivated research to explore (Lewis) catalytic ability of high-entropy oxides for promoting organic transformations in liquid phase. In this research study, we synthesized and characterized four single-phase, cubic structure (*Fm-3m*) ceria-zirconia-rare-earth high-entropy oxides

## Experimental

### Synthesis and structural characterization of the catalysts

Table 1. Synthesized high-entropy oxides

Compound	Chemical formula
CZLEY	Ce <sub>0.2</sub> Zr <sub>0.2</sub> La <sub>0.2</sub> Eu <sub>0.2</sub> Y <sub>0.2</sub> O <sub>2</sub>
CZLPY	Ce <sub>0.2</sub> Zr <sub>0.2</sub> La <sub>0.2</sub> Pr <sub>0.2</sub> Y <sub>0.2</sub> O <sub>2</sub>
CZEYG	Ce <sub>0.2</sub> Zr <sub>0.2</sub> Eu <sub>0.2</sub> Y <sub>0.2</sub> Gd <sub>0.2</sub> O <sub>2</sub>
CZLPG	Ce <sub>0.2</sub> Zr <sub>0.2</sub> La <sub>0.2</sub> Pr <sub>0.2</sub> Gd <sub>0.2</sub> O <sub>2</sub>

Fig. 1.

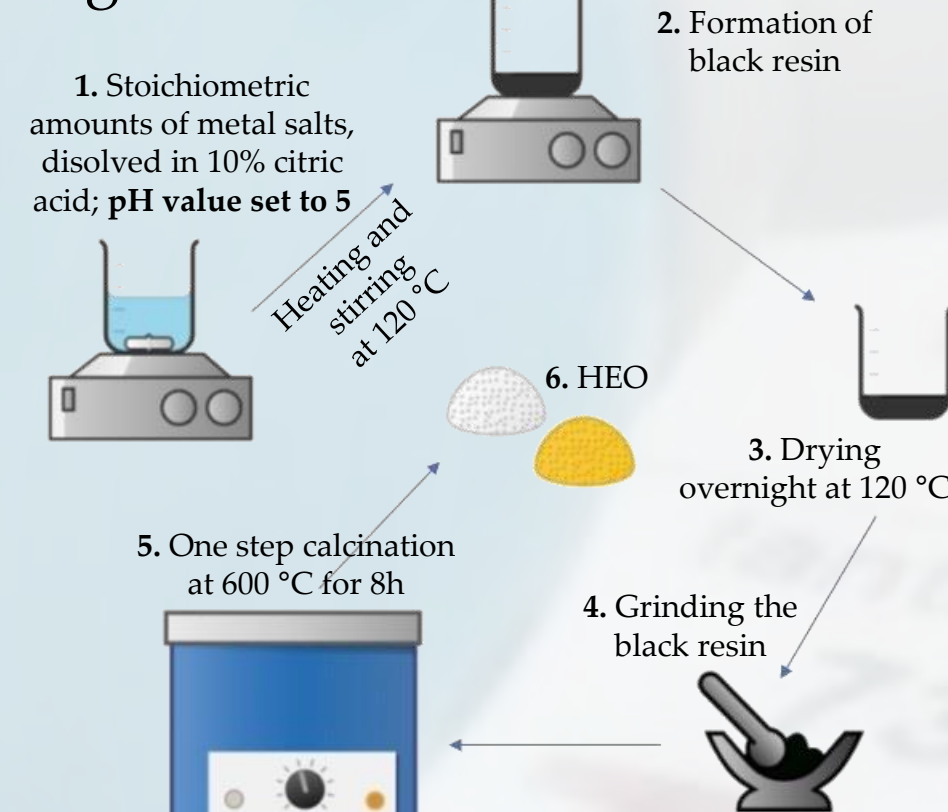


Figure 1. shows a synthetic procedure of modified, aqueous sol-gel citrate route for metal oxides synthesis, while Rietveld output plots reveal phase purities of synthesized catalysts, as shown in Figure 2. Lattice parameters are similar for all catalysts but differ from pure CeO<sub>2</sub>. This shows, the addition of cations, with the same coordination number, and similar ionic radii into a single crystal lattice of CeO<sub>2</sub>, originate expansion of the lattice. Visualized structures are shown in insets for each catalyst.

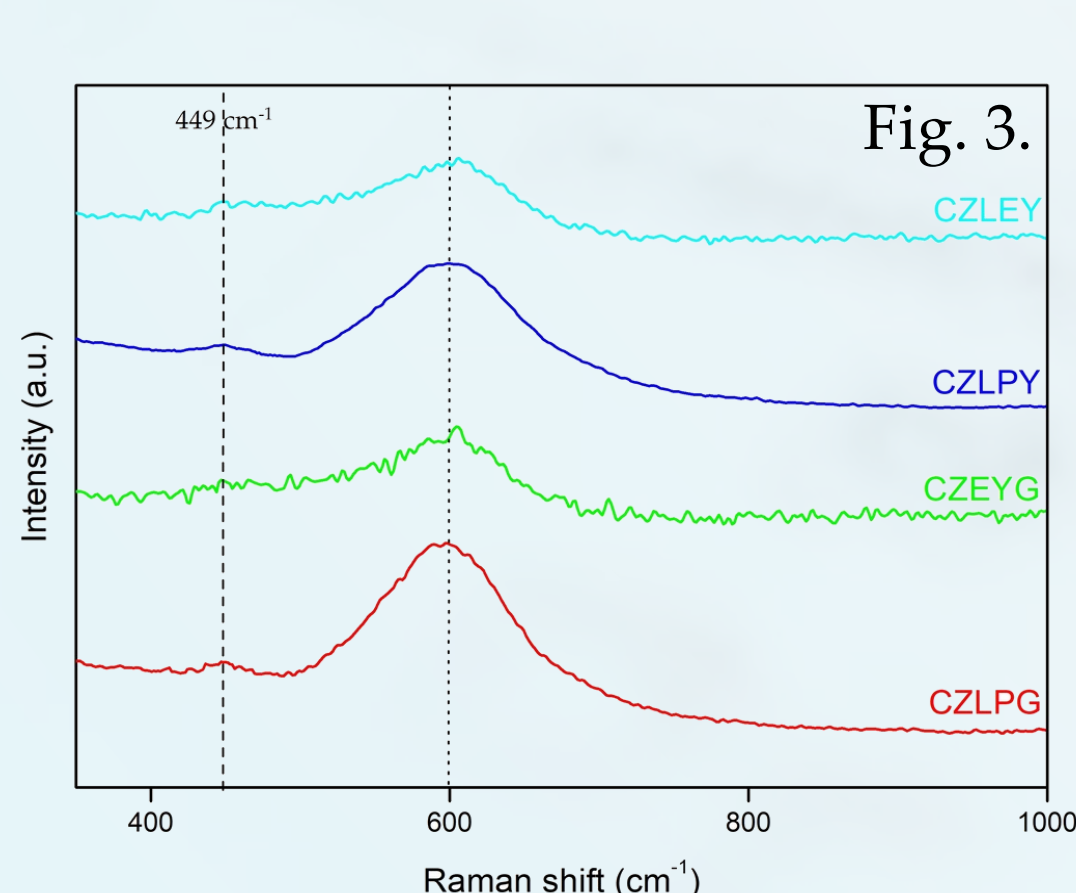
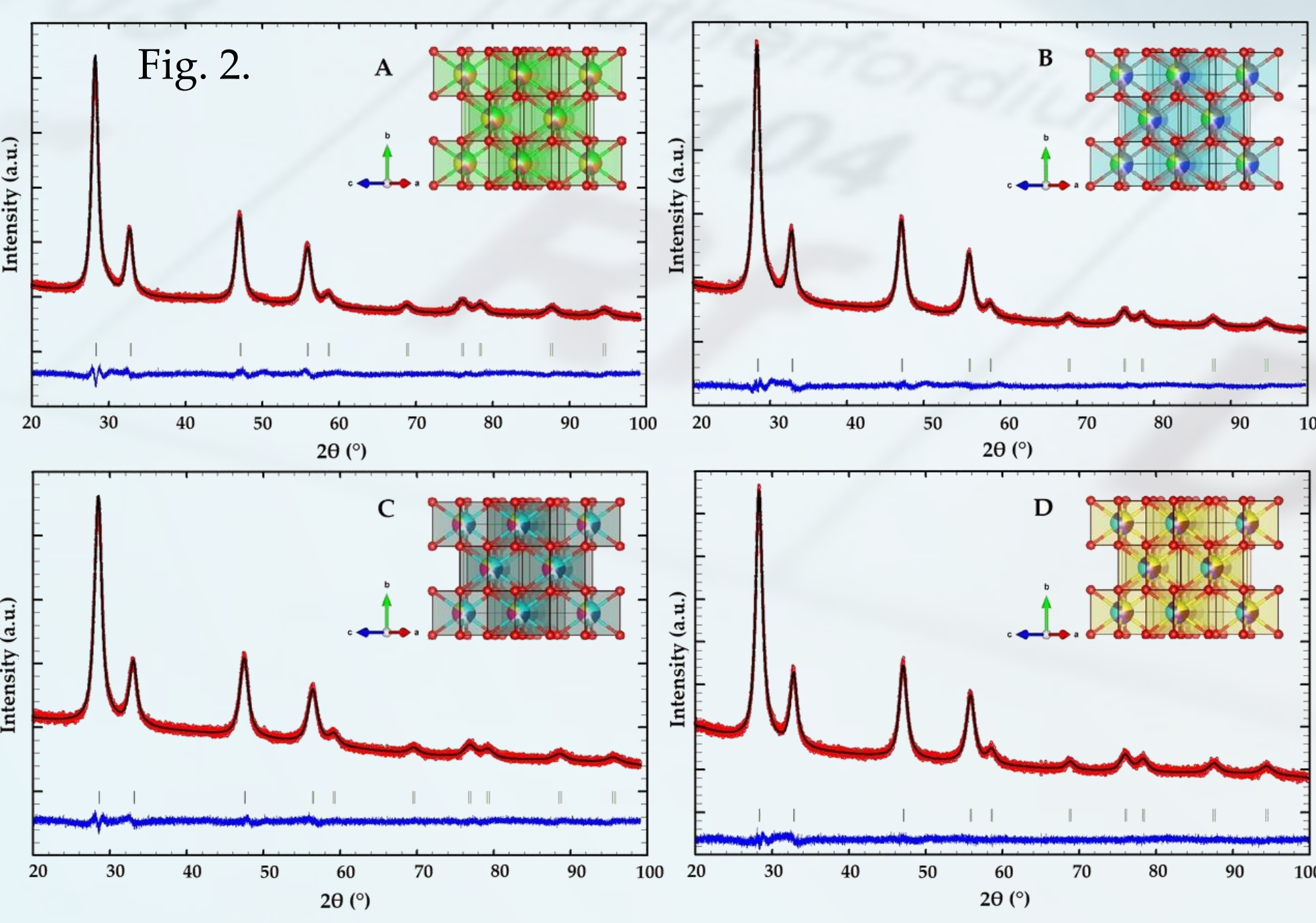
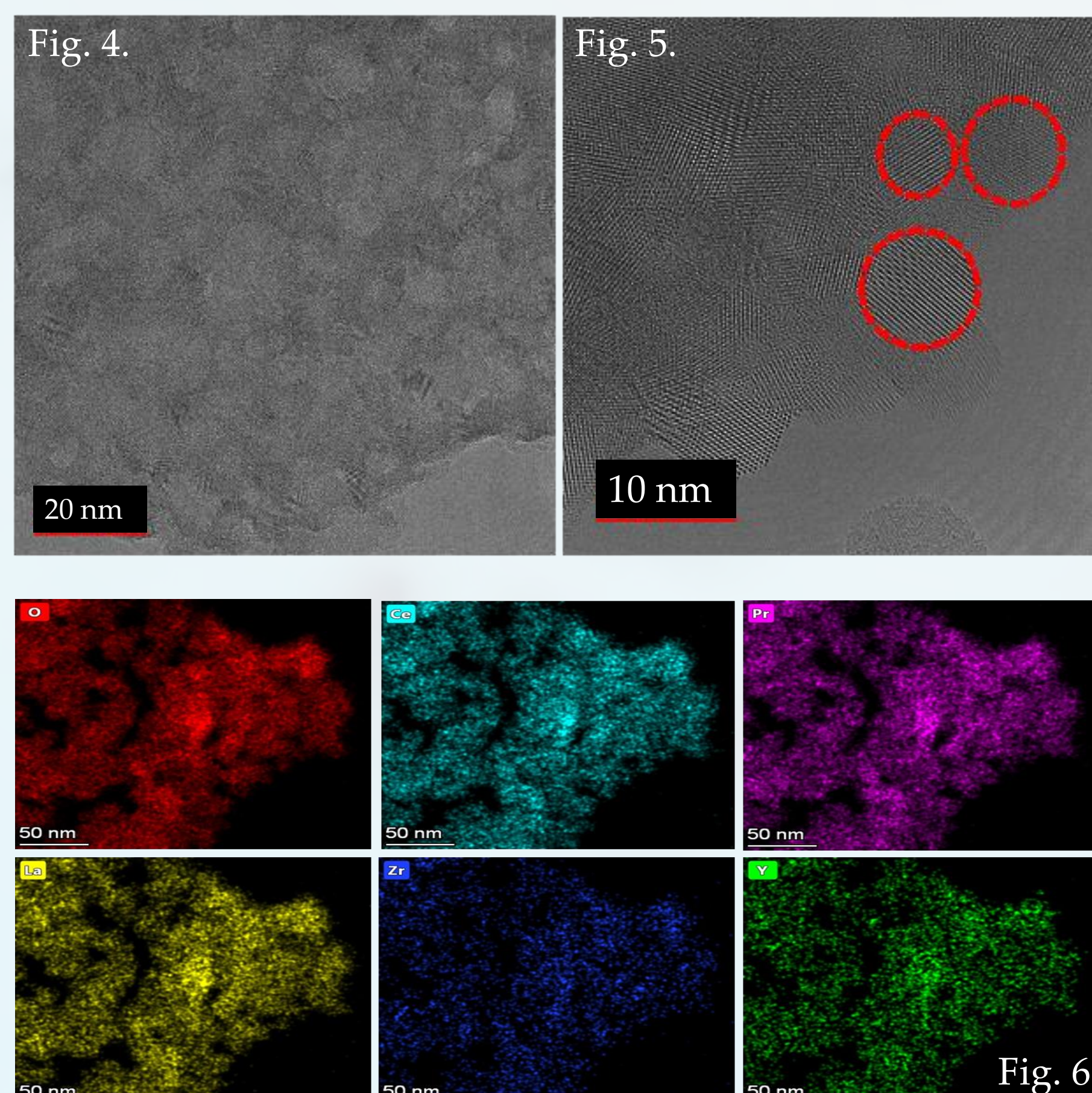


Figure 3. shows Raman spectra of newly synthesized catalysts with  $F_{2g}$  bands at 449 cm<sup>-1</sup>, and defect bands at 600 cm<sup>-1</sup>.

TEM images and EDS elemental maps (Figures 4.-6.) give an insight into morphology and crystallite size and reveal equal distribution of the elements in CZLPY catalyst.



### Catalytic Ability

Table 2. Physico-chemical characteristics of the investigated compounds

Compound	Pore volume (cm <sup>3</sup> /g)	S <sub>BET</sub> (m <sup>2</sup> /g)	Average crystallite size (nm)/XRD	Average crystallite size (nm)/HRTEM	$\Pi_D/\Pi_{F2g}$	Acidity (a.u./g)
CZLEY	0.14	48	6	-	1.30	31
CZLPY	0.27	103	6	6	1.81	77
CZEYG	0.08	51	5	-	1.44	54
CZLPG	0.33	60	6	-	1.90	44

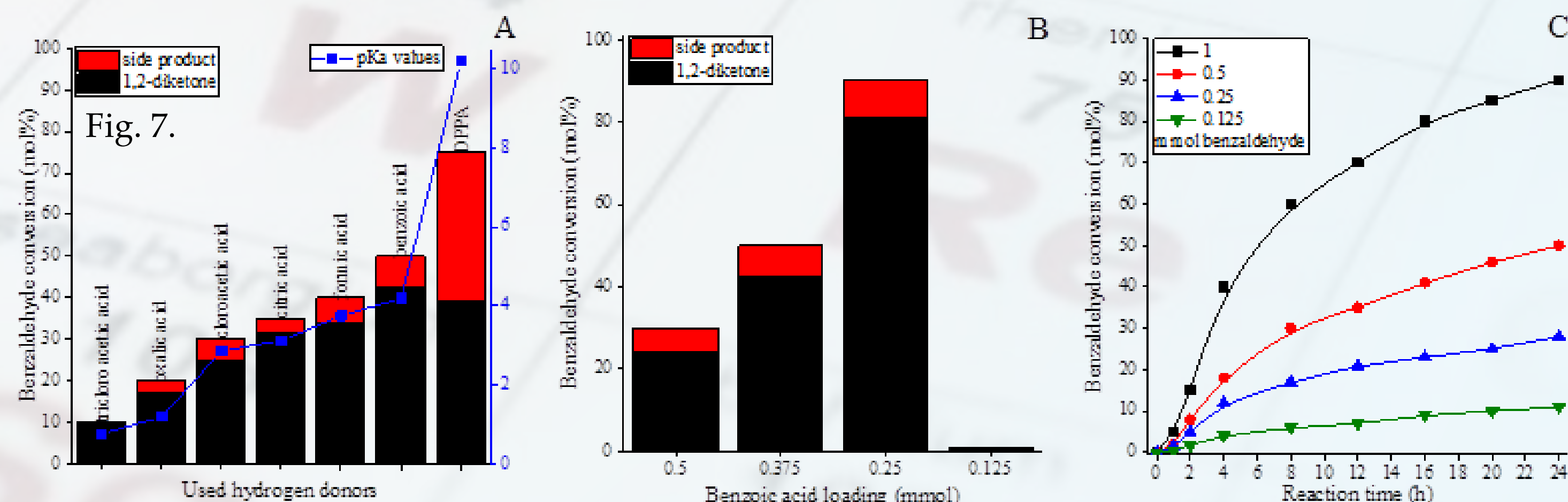


Figure 7. Benzaldehyde conversions as function of the quality of the hydrogen donors (A) and benzoic acid loading (B). Time profiles of benzaldehyde conversions at different benzaldehyde loadings (C). Reaction conditions: 1 mmol benzaldehyde, 2cm<sup>3</sup> acetonitrile, 0.5/0.25 mmol organic acid/benzoic acid, 5 mol% CZLPY catalyst, reflux temperature, 24 h

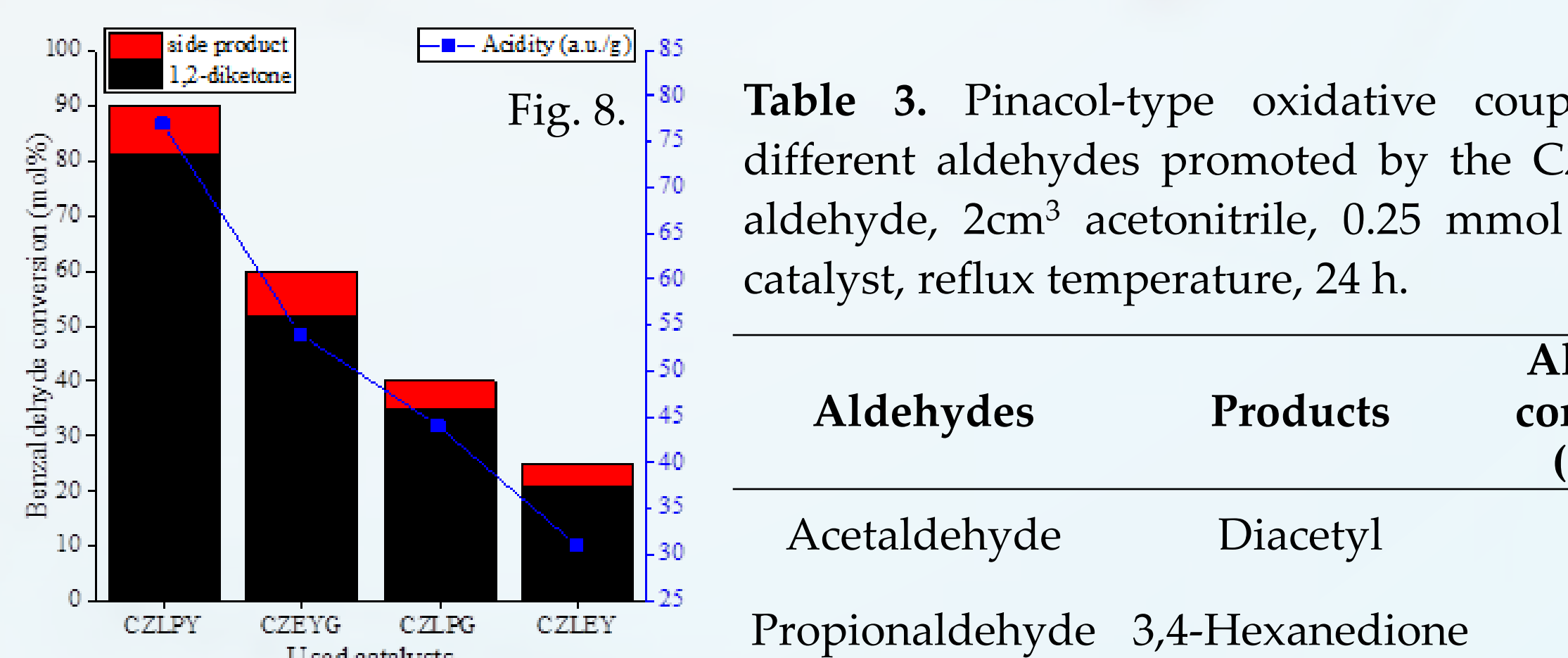


Figure 8. Comparative study on the catalytic ability of the different high-entropy oxides for promoting oxidative Pinacol-type coupling reaction of the benzaldehyde. Reaction conditions: 1 mmol benzaldehyde, 2cm<sup>3</sup> acetonitrile, 0.25 mmol benzoic acid, 5 mol% catalyst, reflux temperature, 24 h.

Table 3. Pinacol-type oxidative coupling reactions of the different aldehydes promoted by the CZLPY catalyst. 1 mmol aldehyde, 2cm<sup>3</sup> 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
Vanillin	Benzo(1,3)dioxol-5-yl-ethane-1,2-dione	67	60

## Conclusions

Four ceria-zirconia-based high-entropy catalysts have been successfully synthesized. The applied synthetic route, called the modified sol-gel citrate route, resulted in phase pure compounds with cubic structure, with lattice parameters that differ from pure CeO<sub>2</sub>, which is related to five cations present into a single crystal lattice. Investigation of physico-chemical properties of newly developed and synthesized catalysts shows that 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 actual catalysts, which demonstrated the catalytic abilities and chemo-selectivity of the catalysts. Upon using HEOs as catalysts, the desired diketone product was produced with almost the same selectivity, unlike activity, that followed the trend of increasing acidity.