

APPLICATION OF CERIA-ZIRCONIA-BASED HIGH-ENTROPY OXIDES AS CATALYSTS IN CONVERSION OF ORGANIC MOLECULES

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INTRODUCTION

Novel high entropy oxides (HEOs) were synthesized in nanocrystalline powder form using a modified citrate sol-gel route. These compounds were further structurally characterized using powder X-ray diffraction (PXRD), Raman spectroscopy, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS), high resolution transmission electron microscopy (HRTEM), BET physisorption measurements, thermogravimetric analysis. HEOs were further used as catalysts for efficient Lewis acid-catalyzed direct conversion of aldehydes to 1,2-diketones in liquid phase. The synergistic effect of various cations incorporated in the same oxide structure (framework) is partially responsible for the efficiency of multi-cationic materials compared to corresponding single-cation oxide forms. Furthermore, a clear, linear relationship between the Lewis acidity and the catalytic activity of the HEOs is observed. Due to the developed strategy, exclusively diketone selective, recyclable, versatile heterogeneous catalytic transformation of aldehydes can be realized under mild reaction conditions.

EXPERIMENTAL

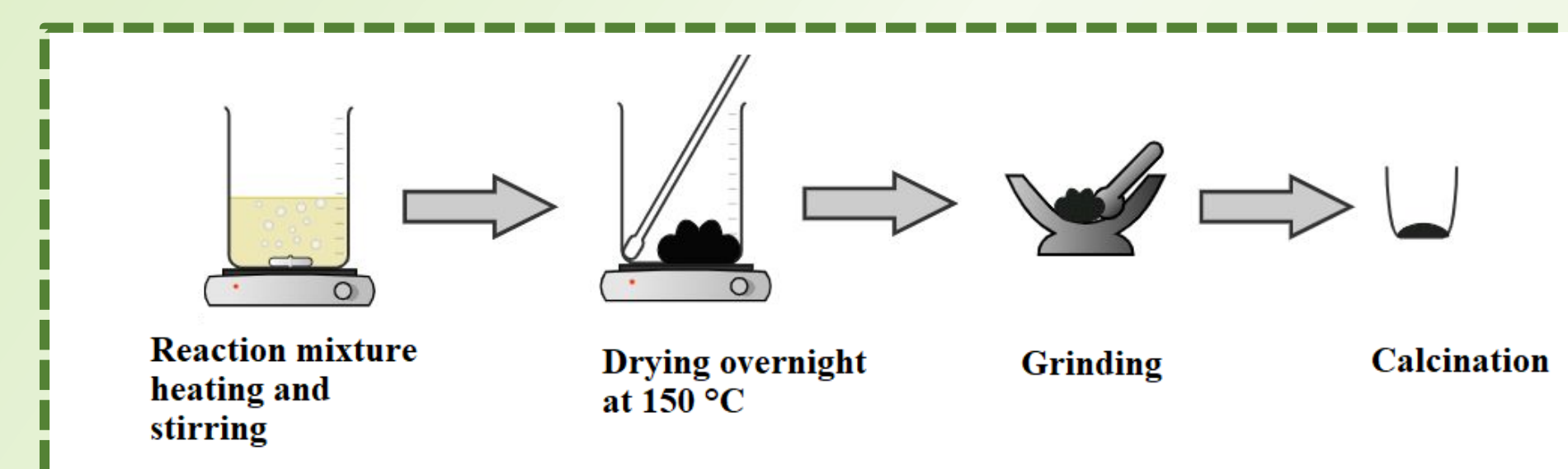


Figure 1. Synthesis procedure for obtaining phase-pure HEOs.

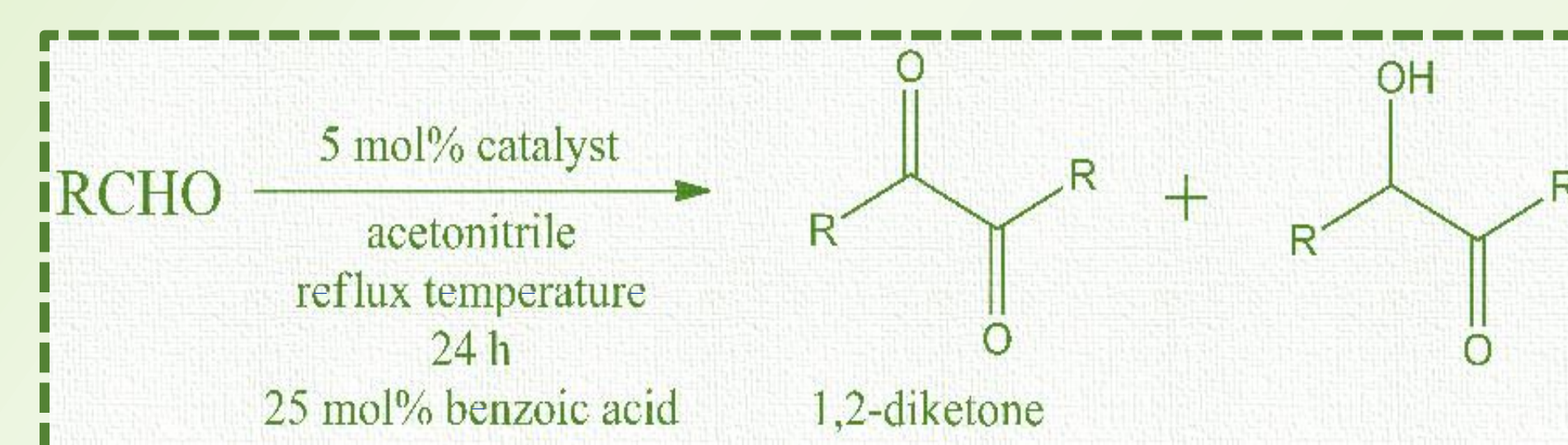


Figure 2. HEO-catalyzed Pinacol-type reaction.

RESULTS AND DISCUSSION

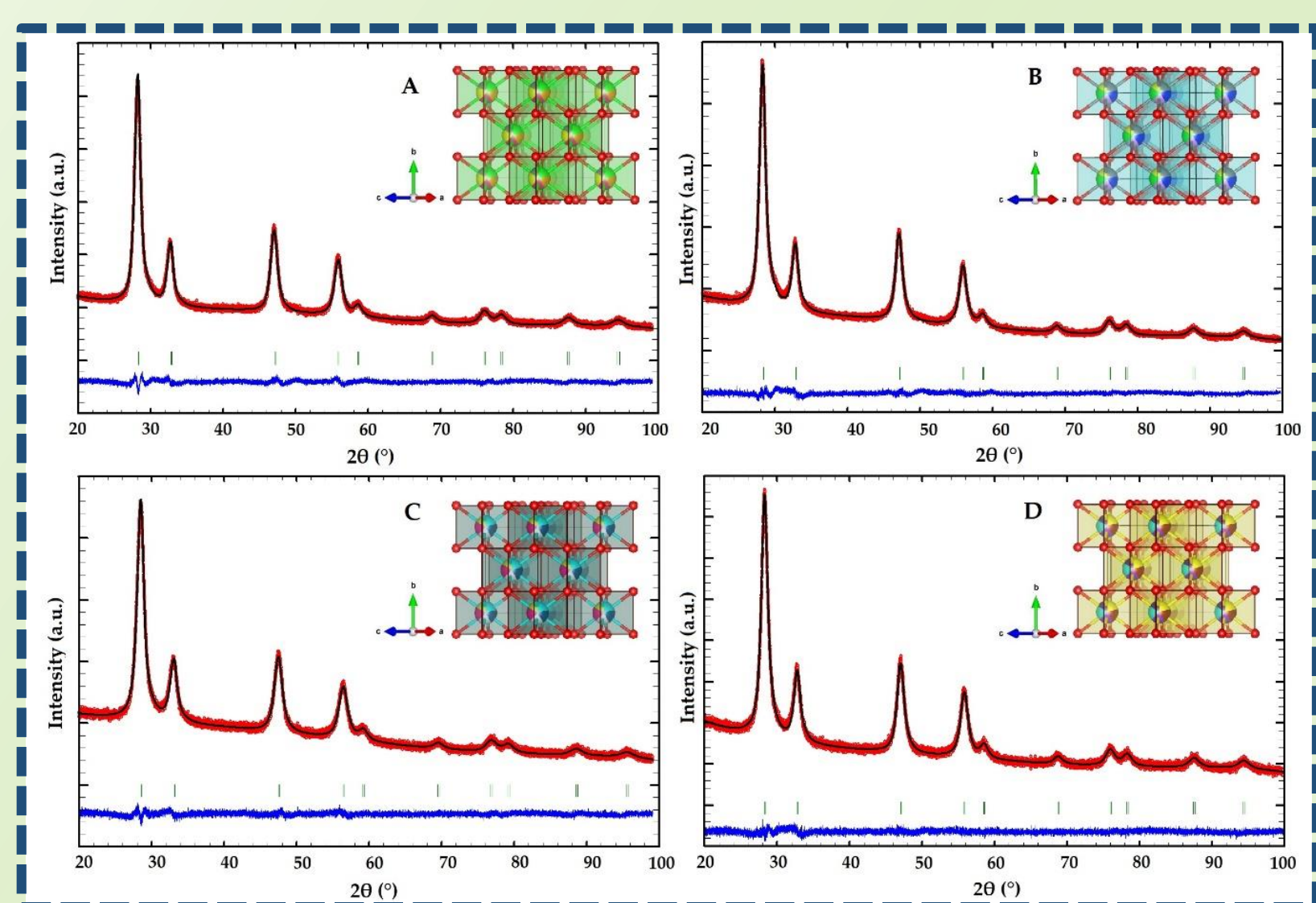


Figure 3. Rietveld plots of the investigated compounds: (A) CZLEY; (B) CZLPY; (C) CZEYG, and (D) CZLPG. Along with Bragg reflections, observed (red), calculated (black) and difference (blue) plots are shown for the fit of the PXRD pattern. In the insets of each figure, fluorite type crystal structure of corresponding HEO is visualized. The average crystallite size is 6 nm for CZLEY, CZLPY, and CZLPG, and 5 nm for CZEYG as calculated by the line broadening method.

Table 1. Physico-chemical characteristics of the investigated compounds.

Compound	Pore volume d (cm ³ /g)	S _{BET} (m ² /g)	Average crystallite size (nm)	Acidity (a.u./g)
CZLEY	0.14	48	6	31
CZLPY	0.27	103	6	77
CZEYG	0.08	51	5	54
CZLPG	0.33	60	6	44

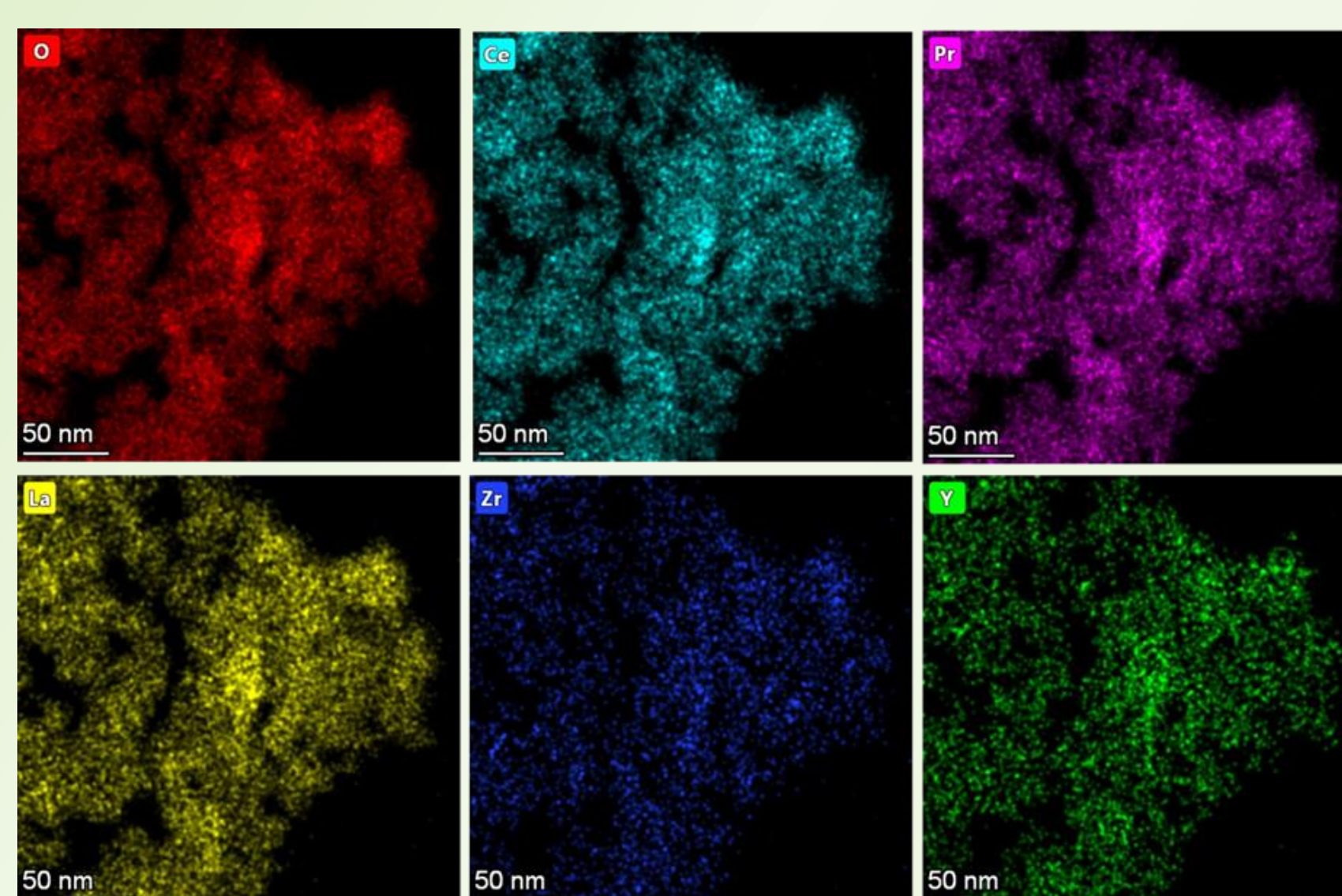


Figure 4. Qualitative EDX elemental maps of CZLPY compound showing uniform distribution of all involved elements.

CONCLUSIONS

The Pinacol-type oxidative coupling reaction of the aldehydes was presented, using HEOs as actual catalysts, which demonstrated the catalytic activities and chemo-selectivity of the catalysts. Reaction conditions were optimized followed by a comparative study on HEOs under the same conditions. 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. The remarkable activity of the HEOs was proven in comparison with pure building block oxides and their physically mixed composites, especially in the case of CZLPY compound. CZLPY oxide proved to be versatile, reusable and heterogeneous catalyst.

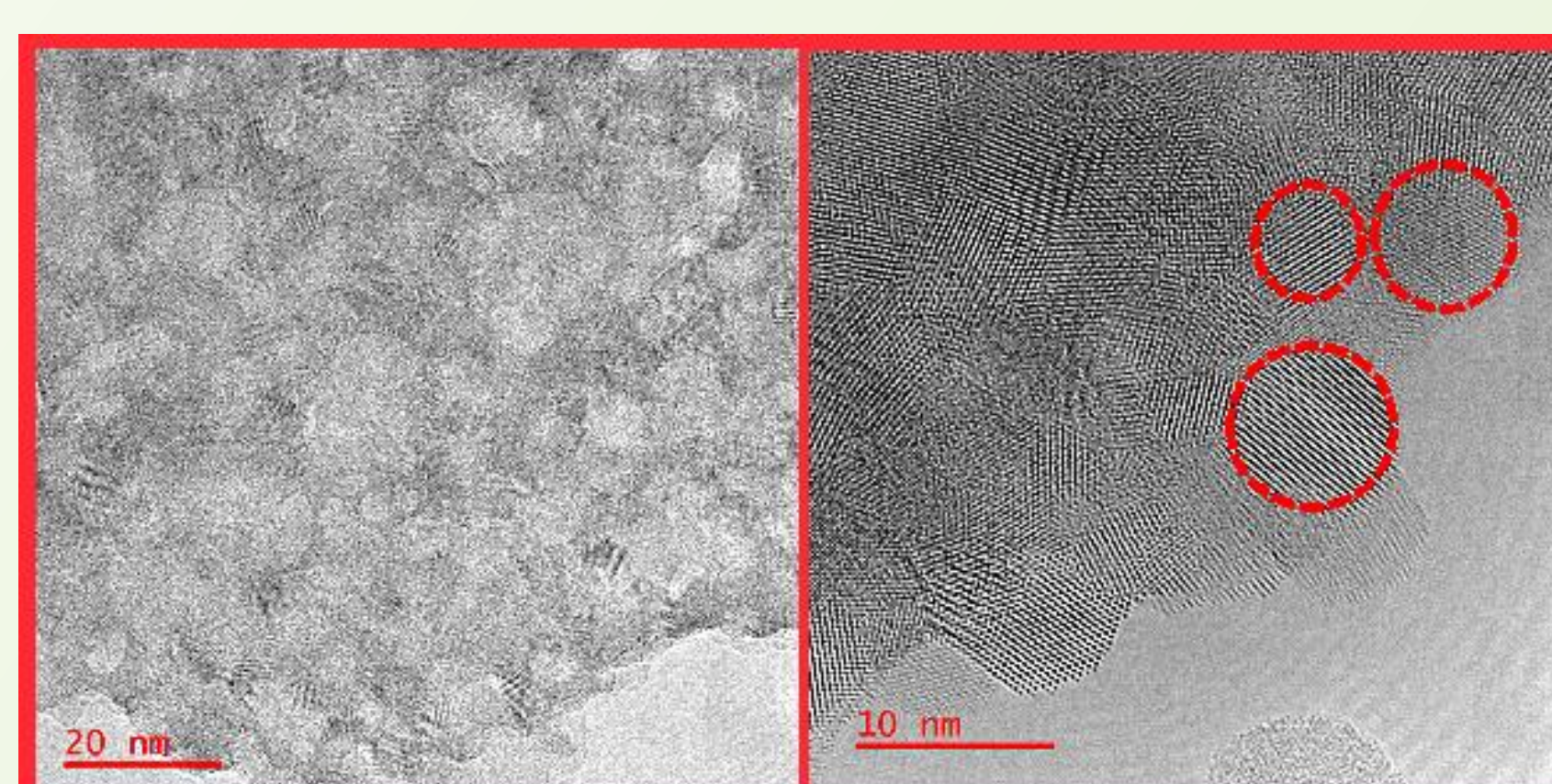


Figure 5. TEM/HRTEM images of CZLPY powder sample at different magnifications showing agglomerated crystallites.

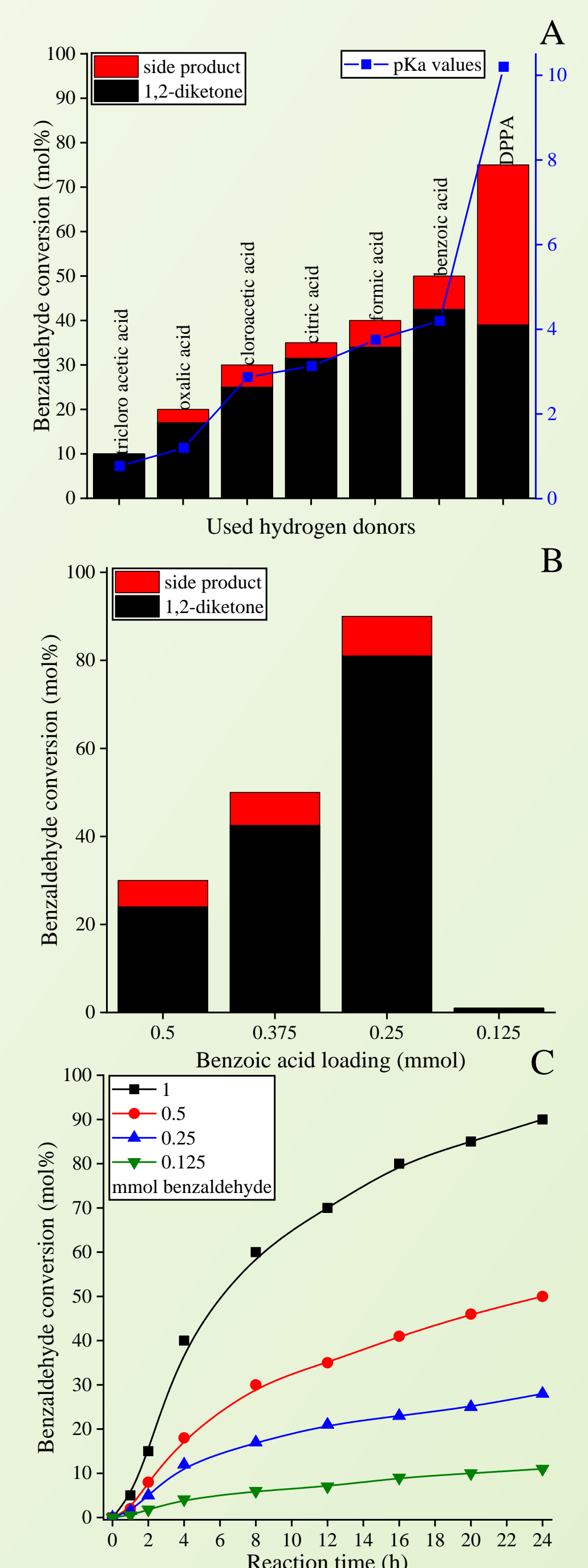


Figure 6. Benzaldehyde conversions as function of the quality of the hydrogen donors (A) and benzoic acid loading (B). Time profiles of benzaldehyde conversions at different benzaldehyde loadings (C). Reaction conditions: 1 mmol benzaldehyde, 2cm³ acetonitrile, 0.5/0.25 mmol organic acid/benzoic acid, 5 mol% CZLPY catalyst, reflux temperature, 24 h.