

Sonohydrothermal Synthesis of Nanotstructured (Ce,Zr)O₂ Mixed Oxides with Enhanced Catalytic Performance

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Supporting Information

Hydrothermal treatment.

Stainless steel made hydrothermal reactor (Fig. S11) with a volume of 50 mL is equipped with PTFE inner vessel and pressure safety valve.

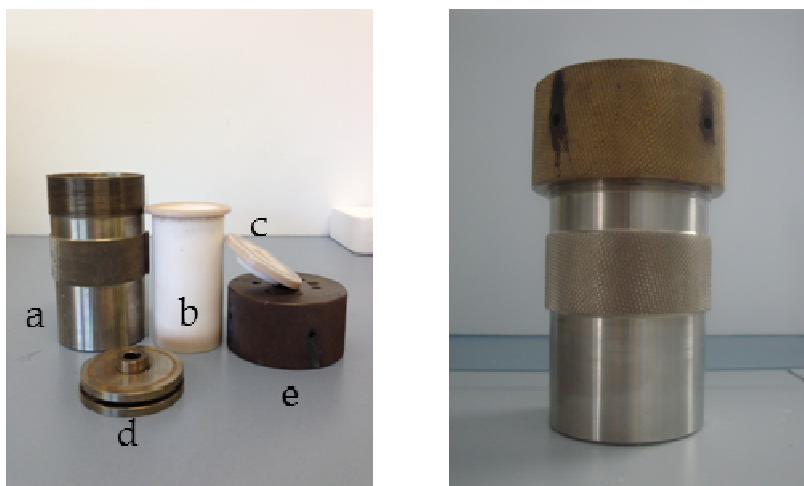


Fig. S11. Homemade 50 mL hydrothermal reactor (left dismantled, right assembled), a and e: stainless recipient and his cover, b and c : Teflon skirt and his cover, d : pressure safety valve

Ultrasonically assisted coprecipitation.

Ultrasonic treatments were carried out within a glass reactor equipped with a 1 cm² titanium probe and piezoelectric transducer supplied by a 20 kHz generator (750 W, Sonics & Materials) shown in Fig. SI2. In all experiments the solution volume was 50 mL insuring that the probe was reproducibly immersed below the surface of the sonicated liquid. The irradiation intensity, $I = 32 \text{ W} \cdot \text{cm}^{-2}$, or the absorbed acoustic power, $P_{ac} = 0.46 \text{ W} \cdot \text{mL}^{-1}$, was assessed by thermal probe method. Temperature at 80°C during the process was provided by ultrasonic heating of irradiated liquid.

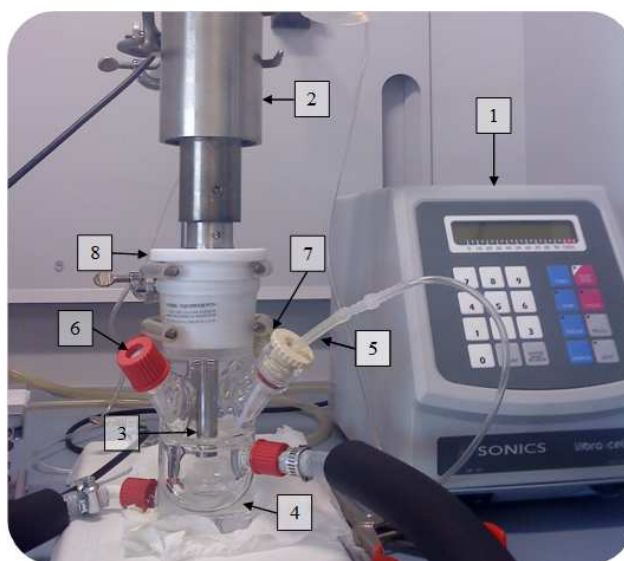


Figure SI2. Experimental set-up for ultrasonic treatment at 20 kHz. 1. Ultrasonic generator of 20 kHz ultrasound with 750 W of maximal electric power, 2. Piezoceramic transducer, 3. Titanium horn, 4. Thermostated reactor, 5. Gas inlet, 6. Sample outlet, 7. Thermocouple, 8. PTFE ring.

Sonohydrothermal treatment.

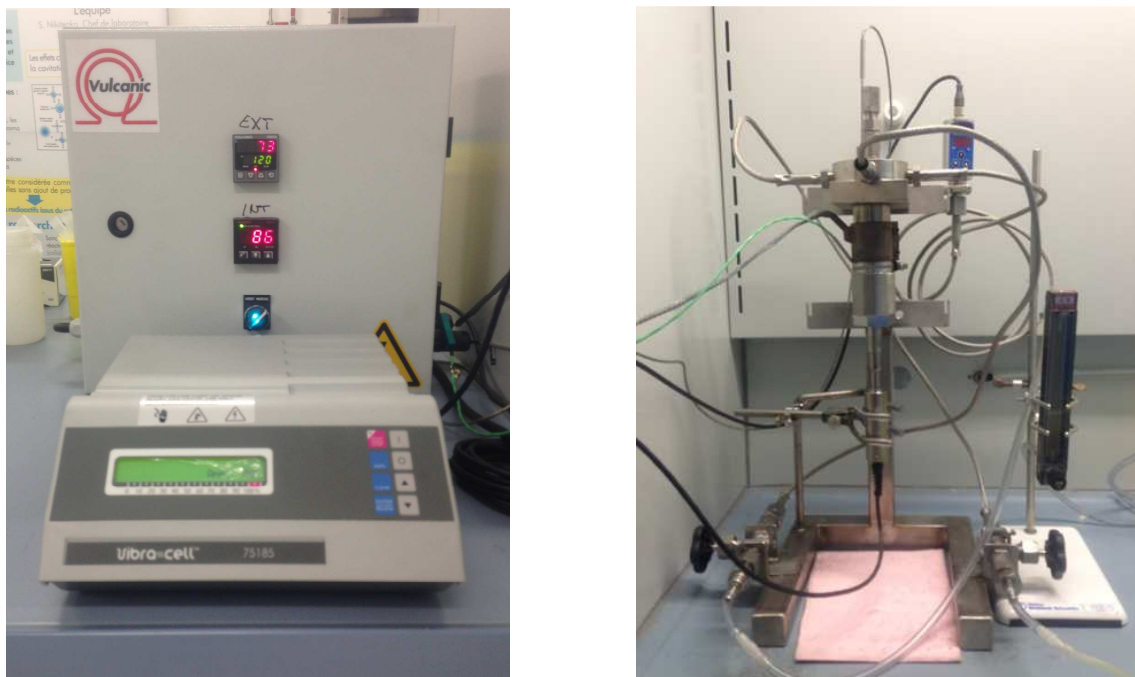


Figure SI3. Photograph of the ultrasonic generator and the control panel.

Analytical procedures

Hydrogen peroxide concentration was monitored by spectrophotometry with Ti(IV) in 0.5 M HNO_3 containing 0.01 M of hydrazine nitrate to remove HNO_2 admixtures from nitric acid ($\lambda = 410 \text{ nm}$, $\varepsilon = 658 \text{ cm}^{-1} \text{ M}^{-1}$).

Gaseous products in the outlet gas were analyzed using a Thermo Scientific VG ProLab Benchtop quadrupole mass spectrometer. The concentration of H_2 was followed with the multiple ion monitoring (MIM) provided by the software. The H_2 formation rate was quantified using external calibration curves prepared with standard gas mixtures (Messer) with a resulting statistical error measured by $\sim 20\%$. The water vapor in the outlet gas was trapped using molecular sieves (Sigma-Aldrich, 3 Å) prior to mass spectrometric analysis.

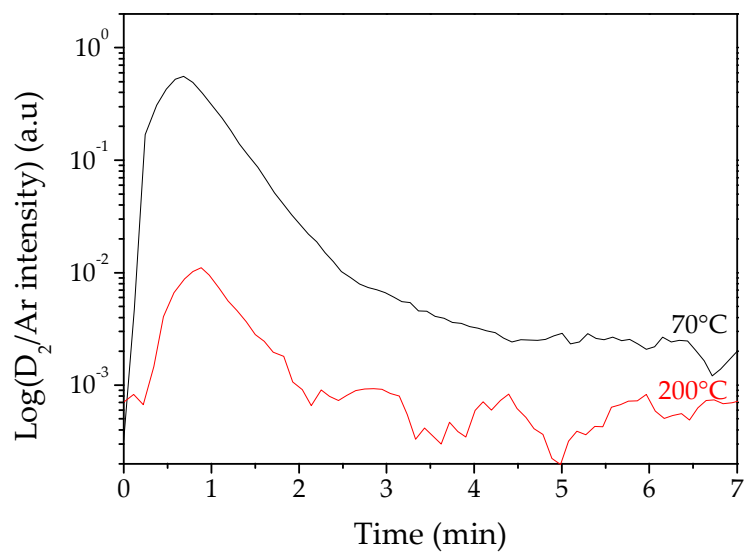


Figure SI4. Mass spectrometric measurements of D_2 released after 3 h of sonohydrothermal treatment at 40% of ultrasonic amplitude.

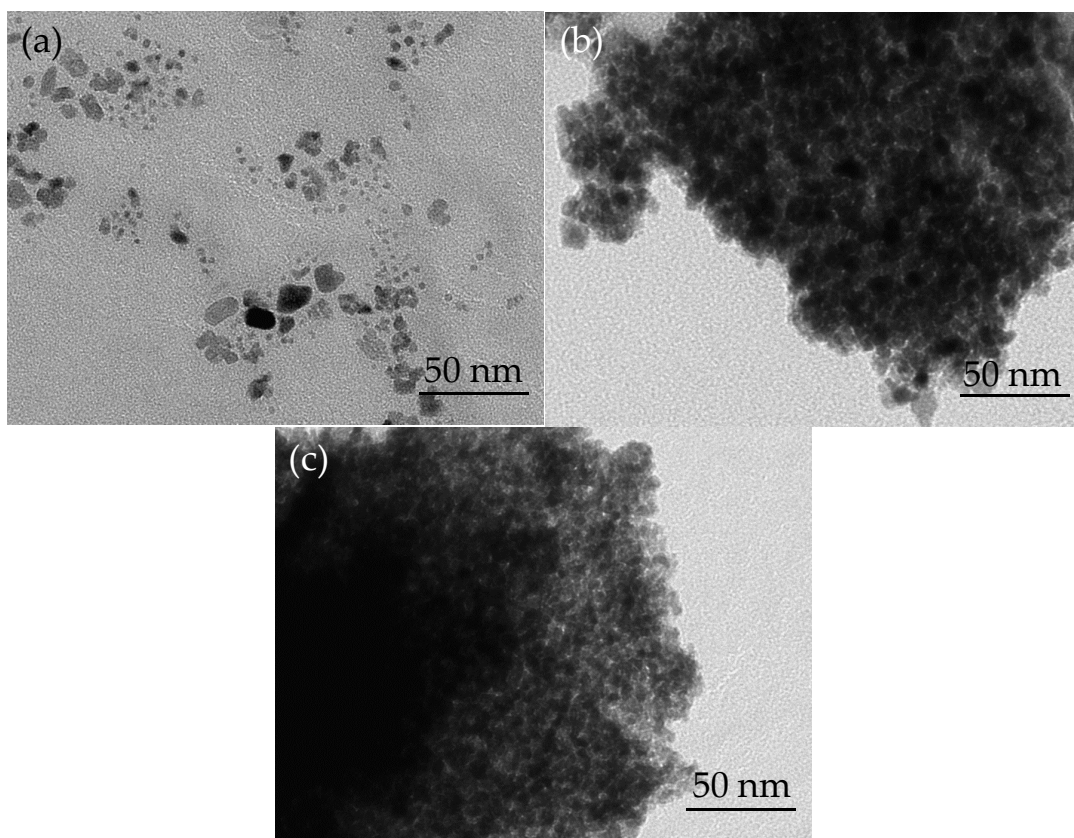


Figure SI5. TEM pictures of heated samples M_{CeZr} (a), S_{CeZr} (b) and H_{CeZr} (c).

Complementary data

Without heat treatment, the support synthesis by the sonohydrothermal method allows to obtain a catalyst which exhibit a catalytic activity closed to the one prepared with the heated sample. Nevertheless, the benefit in catalytic activity with the adjustment of HCOOH concentration is weaker than the one with **Pt/ST_{CeZr}**. Moreover, this material is probably less resistant than a catalyst prepared with a heated support.

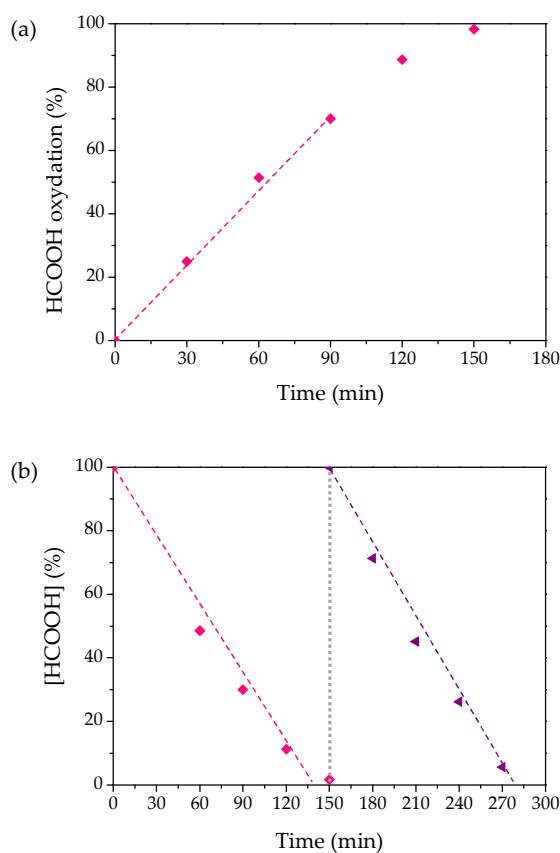


Fig SI6. : (a) Formic acid catalytic oxidation with 0.5 g.L⁻¹ of catalyst **Pt/ST_{CeZr}**^{*} with 1.5 %wt. of Pt ([HCOOH]₀ = 0.1 M), (b) Formic acid concentration with 0.5 g.L⁻¹ of catalyst **Pt/ST_{CeZr}**^{*} with 1.5 %wt. of Pt ([HCOOH]₀ = 0.1 M) ◆, adjustment ▲ of HCOOH concentration, --- [HCOOH] adjustment.

Table SI1. Molar contents of cerium and zirconium measured by EDX method, measured specific surface area (S_{BET} - $\text{m}^2.\text{g}^{-1}$), internal and external surface (S_{int} and S_{ext} - $\text{m}^2.\text{g}^{-1}$) of as prepared $\text{Pt}/\text{ST}_{\text{CeZr}}^*$ and HCOOH oxidation rate ($\mu\text{mol}.\text{min}^{-1}$) in the presence of $\text{Pt}/\text{ST}_{\text{CeZr}}^*$ (1.5%.wt).

Material	x_{Ce}	x_{Zr}	S_{BET}	S_{int}	S_{ext}	Initial HCOOH oxidation rate	
						Adjustment	
						0	1
$\text{Pt}/\text{ST}_{\text{CeZr}}^*$	0.54	0.46	139	133	6	33.07	34.56