Ultrasound-assisted Reductive Dissolution of CeO_2 and PuO_2 in the Presence of Ti Particles

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Fig. S1: SEM pictures observed for CeO_2 samples obtained from Ce(III) oxalate precursors fired at different temperatures: (a.) 600°C, (b.) 1000°C, and (c.) 1400°C.

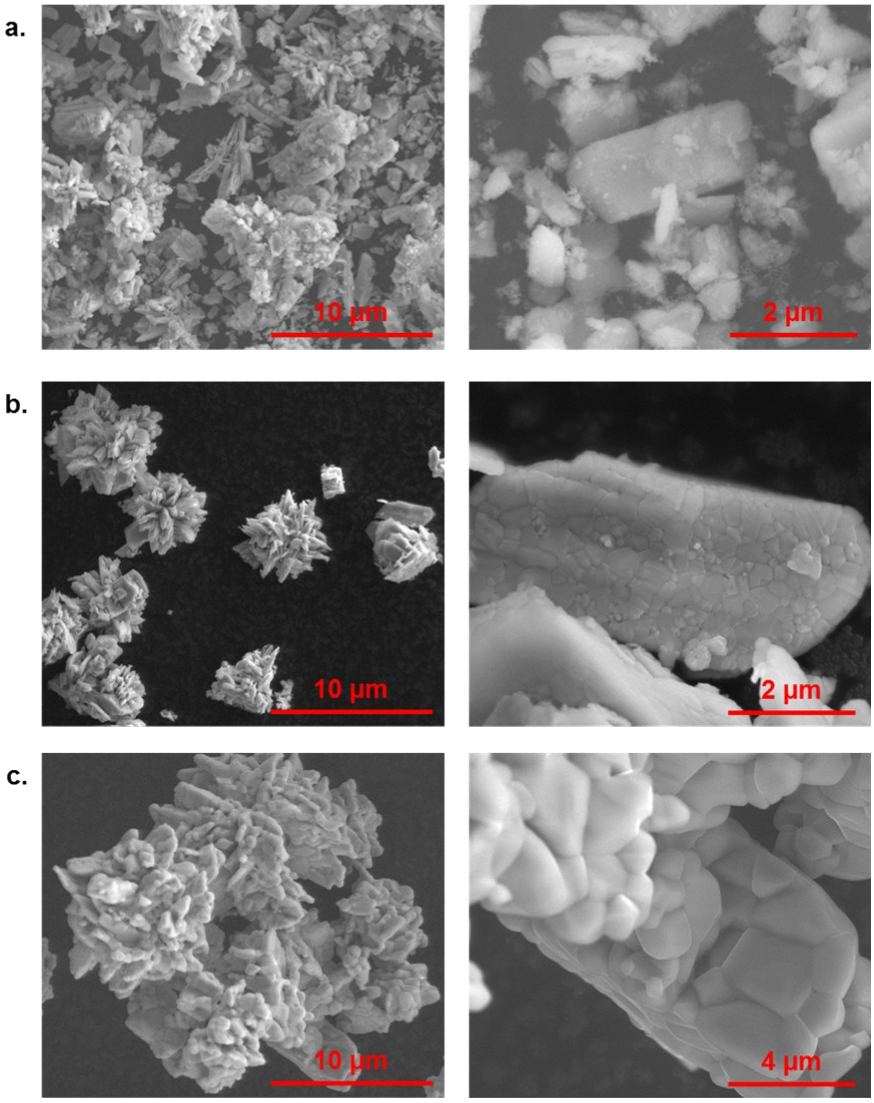
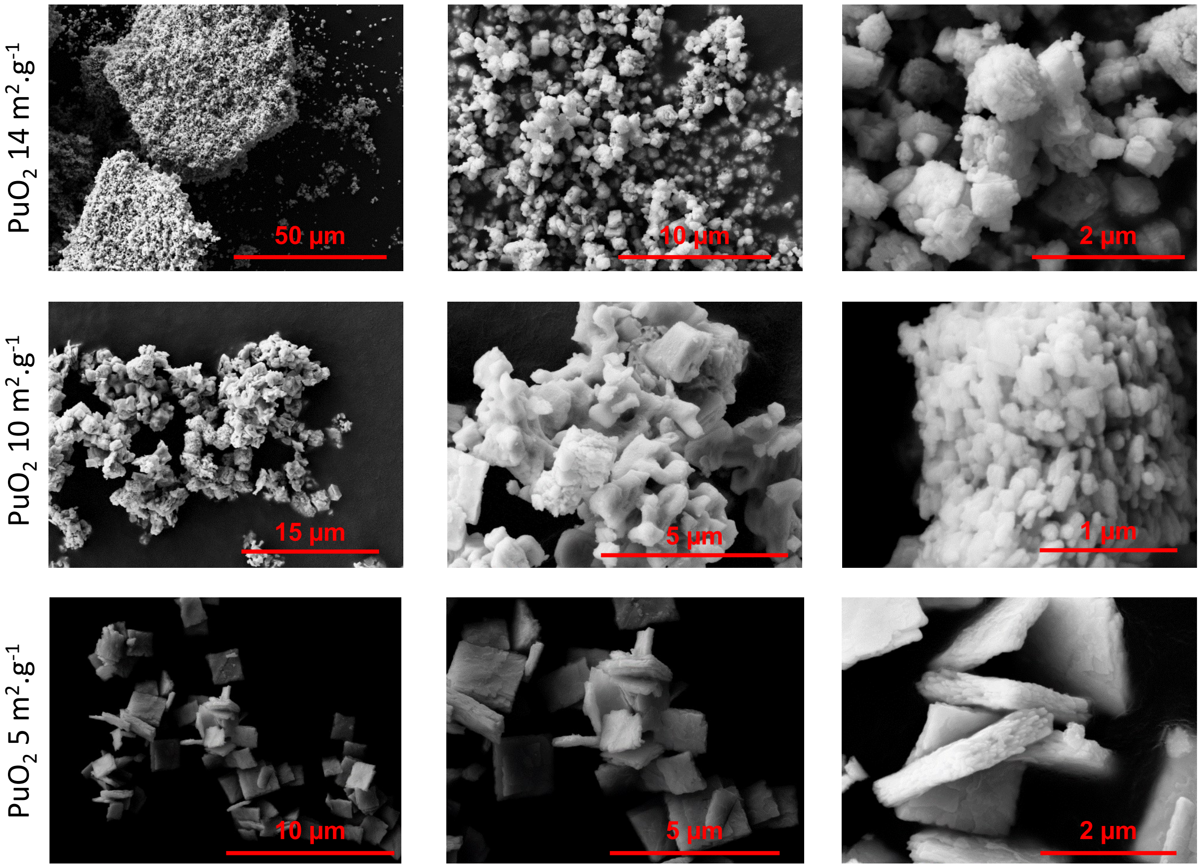


Fig. S2: SEM pictures observed for PuO_2 samples obtained from Pu(IV) oxalates fired at different temperatures: 520°C (14 $m^2.g^{-1}$), 600°C (10 $m^2.g^{-1}$), and 660°C (5 $m^2.g^{-1}$).



Ti granulometry and concentration

Table S1 illustrates the sonochemical dissolution kinetics observed for CeO_2 in 0.5 M HNO_3 / 0.1 M HN / 2 M HCOOH in the presence of Ti powders displaying different granulometries. Before fluoride injection, ceria dissolution rates are found to be increased in the presence of micrometric Ti powders (100 and 325 mesh) with a slightly better yield obtained in 4 h with Ti 100 mesh. These observations are correlated to Ti dissolution which is measured to be about 8.9% and 7.4%, for Ti 100 and 325 mesh, respectively. These observations are in agreement with the above proposed mechanism in which ceria is dissolved by reducing species generated from Ti dissolution. Such results can be relied to the mechanical effect driven by 20 kHz ultrasound. According to the literature, the radius of transient bubbles at 20 kHz is assumed to be about 150 µm at collapse (resonant size). This radius is about the size of Ti 100 and 325 mesh, which explains the observed erosive effect for such particles. The yields observed for Ti dissolution are more important for Ti 325 mesh 3 h after injection of fluorides (the sonotrode contribution is not excluded in this account). Ti 325 mesh appears to offer the best compromise between Ti and CeO_2 dissolutions.

Table S1: Sonochemical (20 kHz, 0.7 W.mL^{-1}, Ar, 33°C) dissolution kinetics observed for ceria (S_{BET}= 15 m^2.g^{-1}) and Ti as a function of Ti granulometry (50 mg) in 0.5 M HNO_3 / 0.1 M HN / 2 M HCOOH. Fluoride injection (10^{-2} M) is performed after 4 h of sonolysis.

Ti	**SSA** (m^2.g^{-1})	**Diameter*** (µm)	**$R_{L,0}$(Ce)**** (g.m^{-2}.min^{-1})	**%Ti dissolved**	
				before injection	*3 h after injection*
100 mesh	< 1	129	3.5 10^{-5}	8.9	67.3
325 mesh	< 1	40	2.6 10^{-5}	7.4	102.7***

*Averaged diameter measured by laser granulometry, $^{**}R_{L,0}$(Ce) is related to ceria dissolution before fluoride injection, ***This high value is attributed to the additional dissolution of the sonotrode.

HNO_3 concentration

The influence of HNO_3 concentration on CeO_2 sonochemical dissolution (in the presence of Ti and fluorides) was evaluated by varying its concentration in 2 M HCOOH / 0.1 M HN. The reductive dissolution of ceria requires a relatively low concentration of nitric acid to be effective (in contrast to the oxidant nature of nitrates). The results reported in Table S2 do not show a clear influence of HNO_3 concentration towards CeO_2 which is almost completely dissolved whatever the experiment. Before fluoride injection, ceria dissolution rate is more important for 1.5 M HNO_3 in agreement with the corresponding Ti observed in solution. This observation confirms the above investigations where the amount of ceria dissolved is shown to be correlated to the quantity of Ti determined in solution. Furthermore, Ti yield observed after dissolution is found to increase with medium acidity. The high values are attributed to the simultaneous dissolution of the Ti sonotrode. It is difficult to discriminate each Ti source; however, these results clearly evidence the ability of the chemical system towards Ti solubilisation (or depassivation). The ability of the system to increase ceria dissolution rates can also be highlighted. In the studied range, Ti dissolution is found to be more important for 1.5 M HNO_3. This observation is in agreement with the literature for diluted media (less than 10 wt.% in HNO_3) where nitrates are described to be not too reactive with Ti surface. Although not really effective after fluoride injection, 1.5 M HNO_3 appears to be more appropriate for initial ceria dissolution in this system.

Table S2: Sonochemical (20 kHz, 0.7 W mL^{-1}, Ar, 50 mg of Ti, 33°C) dissolution kinetics observed in HNO_3 / 0.1 M HN / 2 M HCOOH (V= 50 mL) for ceria (S_{BET}= 15 m^2 g^{-1}) and Ti (325 mesh) as a function of HNO_3 concentration. Fluoride injection (10^{-2} M) is performed after 4 h of sonolysis.

[HNO_3]	**$R_{L,0}$(Ce)*** (g m^{-2} min^{-1})	**%Ce dissolved** (3 h after injection)	**%Ti dissolved**	
			before injection	*3 h after injection*
0.25 M	3.0 10^{-5}	96.5	5.4	57.5
0.5 M	2.6 10^{-5}	95.6	7.4	102.7
1 M	2.5 10^{-5}	100.7	6.9	154.9
1.5 M	4.5 10^{-5}	97.3	16.5	179.6

$^*R_{L,0}$(Ce) is related to ceria dissolution before fluoride injection

Table S3: Sonochemical (20 kHz, 0.7 W.mL^{-1}, Ar, 33°C) dissolution kinetics observed for ceria samples (180 mg) before (240 min of sonication) and 3 h after injection of fluorides (10^{-2} M) in 0.5 M HNO_3 / 0.1 M HN / 2 M HCOOH in the presence of Ti 325 mesh (50 mg). Ceria samples were obtained from Ce(III) oxalate precursors fired at 600°C, 1000°C, and 1400°C.

Calcination temp. (°C)	**Specific surface area** ($m^2.g^{-1}$)	**%Ce dissolved** *before injection*	**%Ce dissolved** *3 h after injection*
600	15	10.8	95.6
1000	~1	6.2	48.4
1400	<1	1.1	14.9

Fig. S3: SEM pictures observed for sonochemical dissolution residues of CeO_2 (fired at 600°C or 1400°C) (a.) before dissolution, (b.) after 4 h dissolution, (c.) after 7 h dissolution. Experimental conditions: sonication (20 kHz, 0.7 $W.mL^{-1}$, Ar, 33°C) of CeO_2 (180 mg) in 0.5 M HNO_3 / 0.1 M HN / 2 M HCOOH in the presence of Ti 325 mesh (50 mg) with injection of NH_4F (10 mM) at 240 min. Large (> 10 µm) particles are attributed to Ti (checked with EDX).

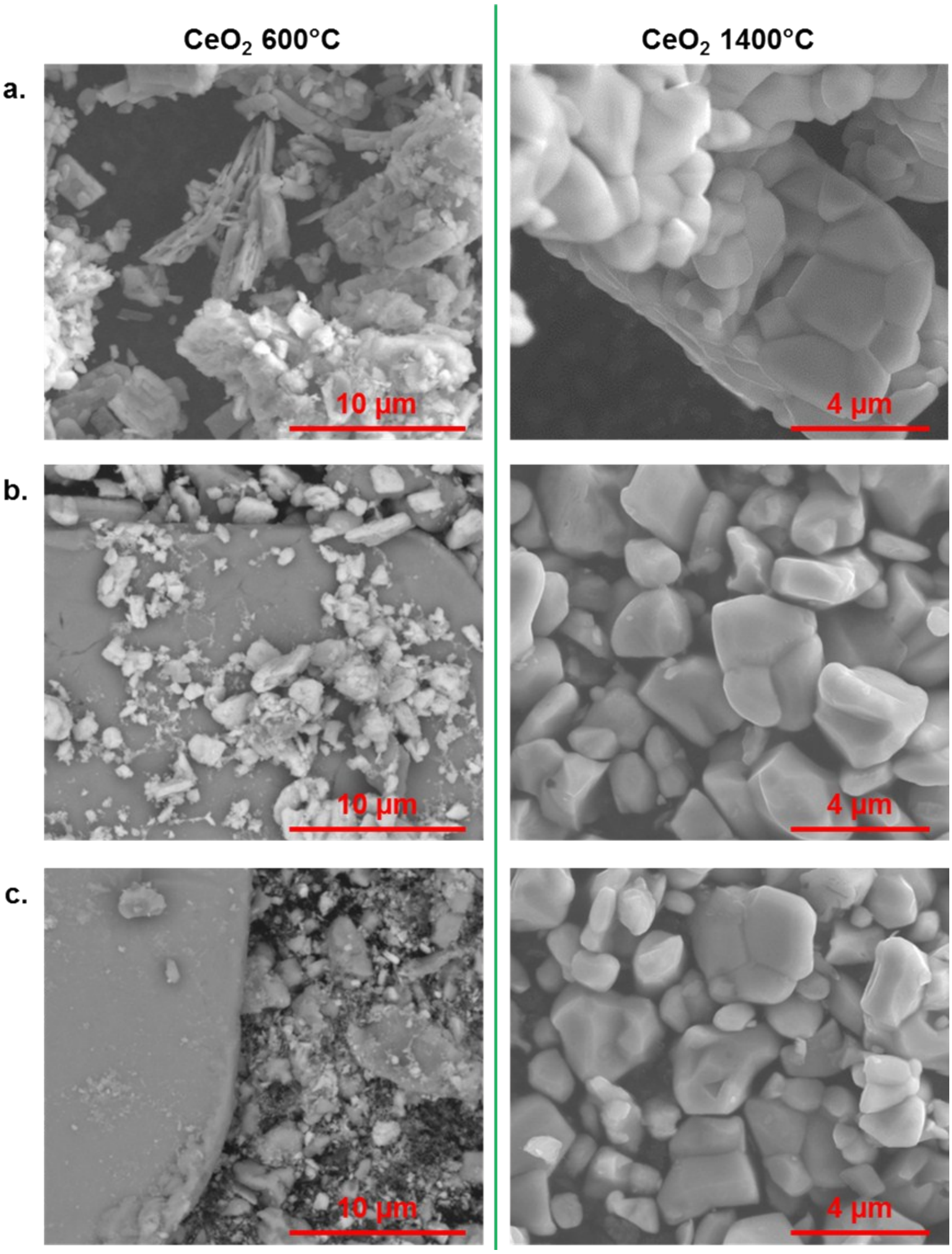


Fig. S4: Sonochemical (20 kHz, 0.45 W mL^{-1}, Ar, 140 mg of Ti 325 mesh, 35°C) dissolution curve obtained for PuO_2 (S_{BET}= 5 m^2 g^{-1}) in 1 M HNO_3 / 0.1 M HN (V= 50 mL) with injection of HF (50 mM) after 30 min of sonication. Insert: corresponding UV-Vis absorption spectra followed by Pu(III) oxidation.

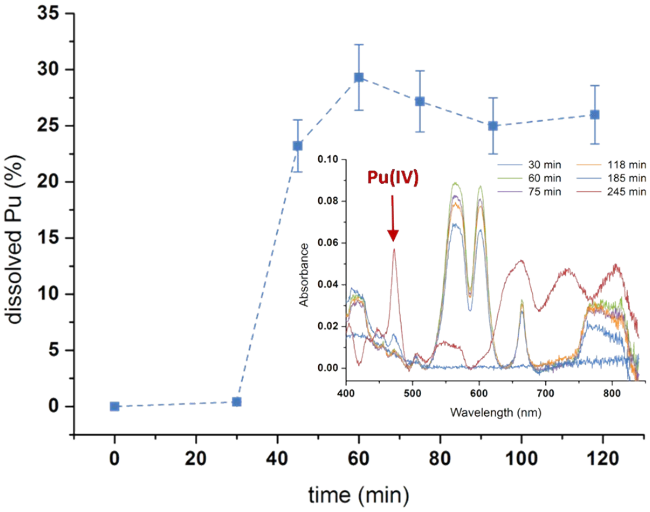


Fig. S5: SEM pictures obtained for PuO_2 dissolution (5 $m^2.g^{-1}$) after 6h30 of dissolution in 1 M HNO_3 / 0.1 M HN at 35°C under stirring (in the presence of Ti particles, 140 mg Ti 325 mesh). NH_4F was injected after 225 min of stirring. Pu appears bright and Ti in dark. (a., b.) are PuO_2 particles. (c., d.) are Ti grains recovered by PuO_2.