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Towards the Green Recycling of Automotive Catalysts with Vitamin C?

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Automotive catalytic converters are composed of a stainless steel casing incorporating a metallic or ceramic honeycomb structure impregnated with a slurry containing the catalyst precursors (washcoat). The catalyst precursors are generally composed of (Ce,Zr)O₂ mixed oxides as oxygen storage promoters on which fine noble metal particles (Pt, Pd, Rh; or PGM for platinum group metals) are previously dispersed.^[1] Due to their versatile applications and the more stringent gas emission legislation, PGM demand is continuously increasing in opposition to the related weakening natural resources. The reprocessing of PGM from spent catalysts is thus gaining more interest and can be currently performed through hydro- or pyrometallurgical processes involving drastic conditions and concentrated reactants.^[2,3] Although efficient, such methods are known to be energy and time consuming, not environmentally friendly, and highly corrosive towards equipment. Selective ceria-based oxide dissolution can represent a promising alternative for the recycling of catalytic converters; such a route could allow the soft release of PGM from the honeycomb matrix and their subsequent recovery by simple separation methods such as centrifugation or filtration. To the best of our knowledge, CeO₂ dissolution has been poorly described in the literature. It is a highly refractive material towards dissolution and its proton-promoted dissolution is not thermodynamically favourable ($\Delta_r G^\circ = 40 \text{ kJ}\cdot\text{mol}^{-1}$). However, in agreement with the high redox potential for Ce(IV)/Ce(III) couple (1.4 V/SHE), reductive dissolution of ceria can be considered.

For the first time, the facile, rapid, and complete reductive dissolution of CeO₂ and cerium-based oxides is reported in very mild conditions at room temperature and pressure. The dissolution procedure requires the combination of ascorbic acid (also known as vitamin C) and a dilute mineral acid. Complete dissolution of ceria and cerium-based oxides can be reached in such conditions providing that a sufficient amount of protons are added to the system (Figure 1). Normalized dissolution kinetics were compared for the various tested oxides as a function of their specific surface area, firing temperature, composition (for mixed oxides), and concentration or nature of the added mineral acid. The complete and congruent (for mixed oxides) dissolution can be observed in 0.5 M ascorbic acid in the presence of dilute nitric, hydrochloric, or sulfuric acid (0.5-3.0 M), for the various oxides and catalyst surrogates investigated in this study. For Pt/CeO₂ samples, Pt, which was found to be very stable in this chemical system, can be separated after complete dissolution of the support.

After rigorous characterisation of the oxides (commercial origin or home-prepared), dissolution progress was evaluated with ICP-OES and SEM techniques. UV-Vis, ESR, and FTIR spectroscopies were then used in order to decipher the dissolution mechanism. The formation of an intermediate and stabilized complex at ceria surface, and the contribution of ascorbate radical in the dissolution mechanism, were confirmed (Figure 1). Due to its simplicity, sustainability, and versatility (compatible with mixed oxides, or high-fired oxides exhibiting low reactivity), this inexpensive and green procedure appears very promising for the recycling of automotive catalytic converters.

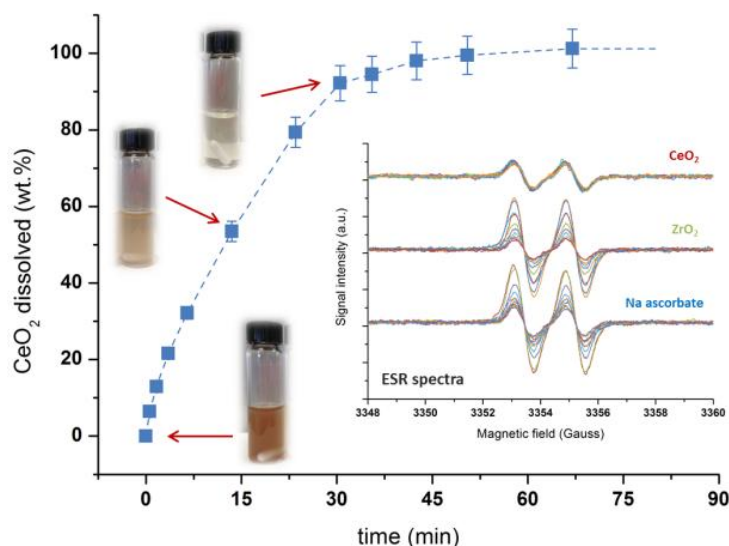


Figure 1: Dissolution kinetic curve observed for CeO₂ (250 m².g⁻¹, 180 mg) in 0.5 M ascorbic acid / 0.75 M HNO₃ (50 mL, 550 rpm, 25°C). Insets: colour evolution of the suspension and ESR spectra evidencing the contribution of ascorbate radical during CeO₂ dissolution.

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