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► **To cite this version:**

Matthieu Viro, Tony Chave, D. Horlait, Nicolas Clavier, Nicolas Dacheux, et al.. Catalytic reductive dissolution of Pt/CeO₂ under mild conditions. 14th meeting of the European Society of Sonochemistry, Jun 2014, Avignon, France. <hal-04765254>

HAL Id: hal-04765254

<https://hal.science/hal-04765254v1>

Submitted on 4 Nov 2024

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Catalytic Reductive Dissolution of Pt/CeO₂ under Mild Conditions

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Platinum deposition at ceria surfaces has been widely used for catalytic processes including automotive three-way catalysts. Each standard catalytic converter may contain from 3 to 7 g of Pt fine particles dispersed on cerium-based oxides.^[1] The rising world demands of CeO₂/Pt catalysts have contributed to the increase of Pt and Ce prices therefore allowing considering their recycling. Ceria is however difficult to dissolve and usually requires very strong conditions using concentrated acids at high temperature. Due to the highly positive redox potential of Ce^{IV}/Ce^{III} couple, one alternative concerns its reductive dissolution. In this work, the reductive dissolution of ceria is investigated in mild conditions at almost room temperature. The dissolution is catalyzed by the sonochemical deposition of Pt nanoparticles (NPs) at the surface of the oxide (Ar, 18 W.cm⁻², 20-40°C, 20 kHz). Typically, H₂PtCl₆ solution (1 mL, 4.5 g.L⁻¹) is injected into the sonicated mixture (50 mL) to reach a 2.5 wt.% of Pt on ceria support (180 mg).^[2] Sonication is performed in HNO₃-HCOOH-[N₂H₅][NO₃], HNO₃-[N₂H₅][NO₃] or H₂SO₄-HCOOH mixtures. After Pt deposition, further dissolution is carried out under ultrasound or mechanical stirring. Dissolution progress is evaluated using UV-Vis spectroscopy, ICP-AES, and SEM.

In the absence of Pt NPs, the dissolution of CeO₂ is found to be very weak even under US. Increasing the temperature to 40°C allows intensifying dissolution rates and shortening the time required to reduce and deposit Pt at ceria surface. In the presence of Pt NPs, dissolution is found to be dramatically enhanced in HNO₃-HCOOH-[N₂H₅][NO₃]. A faster dissolution behavior of ceria is however noted under mechanical stirring: ~30% of CeO₂ are dissolved in 7 h under silent conditions whereas ultrasound allows only ~17%. This phenomenon is attributed to a sonochemically driven denitration process in HNO₃-HCOOH mixture as already reported.^[3] The oxidizing species generated during sonolysis (mainly HNO₂ and OH^o) enable the scavenging of the reducing species and avoid Ce^{IV} reduction. Furthermore, generated NO_x species from HNO₃ sonolysis can be involved in a passivation effect of the Pt catalyst even in HNO₃-[N₂H₅][NO₃] mixture. Denitration can be avoided by replacing H₂SO₄ instead of HNO₃ for dissolution. In sulfuric mixtures (0.125M H₂SO₄-1M HCOOH), the rate observed for Pt^{IV} sonochemical reduction is found to be equivalent to what observed in nitric solutions under stirring; and the initial normalized dissolution rate for CeO₂ is equivalent with and without US. Quantitative dissolution of ceria can be carried out using these conditions; the separation and recycling of platinum may be considered.

References

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