



Catalytic dissolution of ceria–lanthanide mixed oxides provides environmentally friendly partitioning of lanthanides and platinum



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ABSTRACT

The reductive dissolution of cerium–lanthanide mixed oxides was investigated under mild conditions in weakly acid media. The dissolution is catalyzed by platinum nanoparticles (Pt NPs) deposited onto oxide surfaces. The deposition of Pt NPs was performed by sonochemical reduction of Pt(IV). The dissolution efficiency was studied as a function of different parameters such as stirring, sonication at 20 kHz, dissolution media and oxide composition. The quantitative dissolution of these oxides can be performed in 0.25 M HNO₃–1 M HCOOH–0.2 M [N₂H₅][NO₃] and 0.125 M H₂SO₄–1 M HCOOH under stirring at 40 °C in the presence of argon, or in 0.125 M H₂SO₄ under sonication in the presence of Ar–CO gas mixture at 40 °C. In nitric acid solutions mechanical stirring is more efficient than sonication due to the secondary denitration triggered by ultrasound. The incorporation of trivalent (Gd, Nd) or tetravalent (Tb) lanthanides into the ceria matrix resulted in faster dissolution. After dissolution, lanthanides and platinum can be separated by simple filtration. The catalytic dissolution of ceria-based mixed oxides offers a simple way of lanthanide and noble metal partitioning which could appear of interest for catalyst recycling.

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1. Introduction

Ceria-based mixed oxides have attracted much attention as catalysts for automotive exhaust gas treatment (Kašpar et al., 1999, 2003) and for intermediate temperature solid fuel cells (Fergus, 2006). The catalytic performance of ceria is greatly improved by doping with platinum and other noble metals (Hennings and Reimert, 2007; Pozdnyakova et al., 2006). Because of the rising demand for these compounds coupled to their resulting price increase, the recycling of lanthanides and platinum (or other noble metals) from spent catalysts progressively appears as an economically viable solution. The state-of-the-art technology is to melt the ceramic carrier and collect the precious fraction in a liquid metal bath (Binnemans et al., 2013). As the feed material has quite high melting points, huge amounts of energy are required for this process. Hydrometallurgical treatments of the spent catalysts offer the possibility to recycle the valuable metals with less energy and time demands. Consequently, the dissolution behavior of lanthanide mixed oxides appears as an important area of research, but up to date only few papers dealt with this topic (Binnemans et al., 2013). Usually, highly concentrated acids are required to provide the dissolution of refractory

ceria. A recent study of Ce(IV)–Ln(III) mixed oxides dissolution in concentrated HNO₃ solutions revealed that the dissolution rate is strongly modified by the trivalent lanthanide incorporation due to the accumulation of oxygen vacancies in fluorite structure of ceria (Horlait et al., 2012).

The reductive dissolution of ceria-based systems seems to be an interesting alternative since Ce(III) compounds are much more soluble compared to those of Ce(IV) and the conditions used such as acidity and temperature could be far less aggressive. Several studies of CeO₂ dissolution accompanied with Ce(IV) to Ce(III) reduction have been reported in the literature, involving ascorbic acid (Tamilmani et al., 2005), hot HCl (Lemont, 2008) and HCOOH (Jacobs et al., 2005). In any case, the resulting dissolution rates remained quite low and reached few percents of dissolution. Power ultrasound was shown to enhance the dissolution of CeO₂ in different reductive media, including H₂O₂ and HCOOH-based mixtures (Juillet et al., 1997). However, the dissolution yields remained too low to consider any direct application. Very recently it was shown that Pt nanoparticles (Pt NPs) catalyze the reductive dissolution of CeO₂ in diluted HNO₃ or H₂SO₄ (Viot et al., 2012). This paper is focused on a kinetic study of catalytic reductive dissolution of (Ce_{1-x}Ln_x)O_{2-y} mixed oxides, where Ln is Gd(III), Nd(III) and Tb(IV), in the presence of Pt NPs at almost room temperature. Furthermore, the modification of morphology of mixed oxides and Pt NPs was investigated during dissolution.

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Table 1

Initial normalized dissolution rates of CeO₂, (Ce_{0.8}Gd_{0.2})O_{1.9} and (Ce_{0.8}Tb_{0.2})O₂ under ultrasound (20 kHz, 0.35 W·mL⁻¹, Ar) in the absence of Pt NPs.

Solution	T (°C)	R _{Ce} (×10 ⁻⁵ g·m ⁻² ·min ⁻¹)	R _{Ln} /R _{Ce}
CeO ₂ 600 °C (S _{BET} = 15 m ² ·g ⁻¹) 0.125 M H ₂ SO ₄	40	0.39	–
(Ce _{0.8} Gd _{0.2})O _{1.9} 500 °C (S _{BET} = 29 m ² ·g ⁻¹) 0.25 M HNO ₃ –1.0 M HCOOH–0.2 M [N ₂ H ₅][NO ₃]	20 40	0.06 0.49	1.37 1.19
(Ce _{0.8} Tb _{0.2})O ₂ 500 °C (S _{BET} = 31 m ² ·g ⁻¹) 0.25 M HNO ₃ –1.0 M HCOOH–0.2 M [N ₂ H ₅][NO ₃]	20	0.13	1.39

The statistical error for R_{Ce} measurements was estimated to be equal to 10–15%.

2. Experimental section

2.1. Materials

Commercial reagents from Sigma-Aldrich, VWR, and Strem Chemicals with ≥99.9% purity were used in the experiments. Solutions were prepared using deionized Milli-Q water which had a resistivity higher than 18.2 MΩ·cm at 25 °C. Hydrazinium nitrate, [N₂H₅][NO₃], was prepared by careful neutralization of hydrazine hydrate with pre-diluted HNO₃ acid under vigorous stirring. Cerium–lanthanide mixed oxides were obtained by the calcination in air of Ce(III)–Ln(III) oxalate precipitated from HNO₃ solutions as described in the literature (Horlait et al., 2011). For comparative experiments, pure ceria was prepared by

the same oxalic precipitation protocol then calcinated at 600 °C. The chemical composition and specific surface areas of the obtained powders are summarized in the Tables 1 and 2. They are composed of polycrystalline micrometric slat-shape aggregates with an average length of a few micrometers, and associated thickness of about 100 nm, as reported in the literature (Horlait et al., 2011). The powder XRD diagrams of lanthanide mixed oxides showed the characteristic patterns of the fluorite structure (*Fm* $\bar{3}$ *m*), in agreement with crystalline CeO₂ (JCPDS file 01-081-0792). The only exception concerned Ce_{0.4}Nd_{0.6}O_{1.7}, which exhibited the cubic superstructure (bixbyite, space group *Ia* $\bar{3}$). All these results are in agreement with the literature (Horlait et al., 2012). It is to notice that contrary to Gd and Nd, and similarly to Ce, Tb can be present at +IV oxidation state in the oxide, and can be solubilized through a reductive dissolution way to its +III oxidation state. In this work, Tb was used to assess the influence of the redox properties of the incorporated element on the dissolution kinetics and yields.

2.2. Reactor setup and dissolution procedure

The dissolution experiments were performed in a home-made glass reactor equipped with a jacketed system for temperature control under the effect of ultrasound and magnetic stirring. A 20 kHz ultrasonic horn was immersed vertically at a reproducible distance into the glass cell, and maintained by a airtight Teflon ring. A magnetic stirrer was added to the cell for experiments under mechanical stirring. Ultrasound was generated by a VCX 750 W processor (Sonics & Materials) composed of a piezoelectric transducer and a 1 cm² titanium tip. All experiments were carried out at a steady temperature of 40 °C, controlled with a

Table 2

Initial normalized dissolution rates of ceria-based oxides in the presence of Pt NPs (2.5 wt.%) at 40 °C in argon.

Solution	Conditions	R _{Ce} (×10 ⁻⁵ g·m ⁻² ·min ⁻¹)	R _{Ln} /R _{Ce}	% Ce dissolved after ~7 h
CeO ₂ 500 °C (S _{BET} = 54 m ² ·g ⁻¹) 0.25 M HNO ₃ –1.0 M HCOOH–0.2 M [N ₂ H ₅][NO ₃]	Stirring	2.6 ^a	–	30
	Ultrasound	1.0 ^a	–	18
0.125 M H ₂ SO ₄ –1.0 M HCOOH	Stirring	1.6 ^a	–	23
	Ultrasound	1.5 ^a	–	20
CeO ₂ 600 °C (S _{BET} = 15 m ² ·g ⁻¹) 0.125 M H ₂ SO ₄ –Ar/CO gas mixture (10% of CO)	'US 3 h'	0.75	–	10
	'Full US'	3.2	–	17
CeO ₂ 1000 °C (S _{BET} = 1.5 m ² ·g ⁻¹) 0.25 M HNO ₃ –1.0 M HCOOH–0.2 M [N ₂ H ₅][NO ₃]	Ultrasound	7.2 ^a	–	3
(Ce _{0.8} Tb _{0.2})O ₂ 500 °C (S _{BET} = 31 m ² ·g ⁻¹) 0.25 M HNO ₃ –1.0 M HCOOH–0.2 M [N ₂ H ₅][NO ₃]	'US 1 h'	0.3	1.5	4
	'US 3 h'	8.3	0.9	40
	'Full US'	3.0	1.0	22
(Ce _{0.8} Gd _{0.2})O _{1.9} 500 °C (S _{BET} = 29 m ² ·g ⁻¹) 0.25 M HNO ₃ –1.0 M HCOOH–0.2 M [N ₂ H ₅][NO ₃]	'US 1 h'	0.4	1.0	6
	'US 3 h'	11.3	0.9	43
	'Full US'	1.4	1.1	13
0.125 M H ₂ SO ₄ –1.0 M HCOOH	'US 3 h'	2.9	1.1	24
	'Full US'	3.0	1.0	24
(Ce _{0.7} Nd _{0.3})O _{1.85} 1000 °C (S _{BET} = 3.6 m ² ·g ⁻¹) 0.25 M HNO ₃ –1.0 M HCOOH–0.2 M [N ₂ H ₅][NO ₃]	'US 3 h'	43	1.2	30
	'Full US'	10.4	1.2	14
(Ce _{0.6} Nd _{0.4})O _{1.8} 1000 °C (S _{BET} = 4.8 m ² ·g ⁻¹) 0.25 M HNO ₃ –1.0 M HCOOH–0.2 M [N ₂ H ₅][NO ₃]	'US 3 h'	26	1.2	26
	'Full US'	14	1.1	19
0.125 M H ₂ SO ₄ –1.0 M HCOOH	'Full US'	45	1.1	44
0.125 M H ₂ SO ₄ –Ar/CO gas mixture (10% of CO)	'Full US'	34	1.0	40
(Ce _{0.4} Nd _{0.6})O _{1.7} 1000 °C (S _{BET} = 4.0 m ² ·g ⁻¹) 0.25 M HNO ₃ –1.0 M HCOOH–0.2 M [N ₂ H ₅][NO ₃]	'Full US'	417	1.2	94

For 'US 1 h' and 'US 3 h' experiments, R_{Ce} was measured at mechanical stirring.

^a Literature data (Virot et al., 2012).

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