



Mechanochemical destruction of perfluorinated pollutants and mechanosynthesis of lanthanum oxyfluoride: A Waste-to-Materials process



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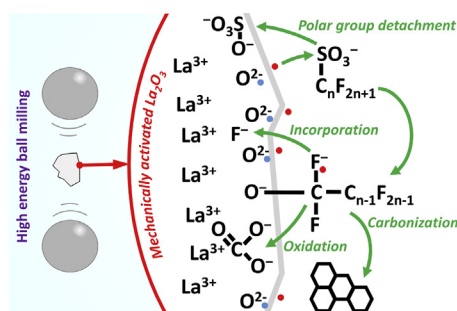
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HIGHLIGHTS

- Perfluorinated chemicals are entirely and safely mineralized.
- Nano-crystalline lanthanum oxyfluoride is the sole main product of the MC reaction.
- Carbonization and oxidation mechanisms differ in oxide anion octet restoration way.
- MC activation of La_2O_3 follows a zeroth-order kinetic.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 November 2016

Received in revised form 19 January 2017

Accepted 8 February 2017

Available online 10 February 2017

Keywords:

Ball milling
Mechanochemistry
Oxyfluoride
Perfluorinated chemicals

ABSTRACT

Perfluorinated chemicals (PFCs) are attracting increasing concern due to their chemical stability and toxicity, which make them classifiable as persistent organic pollutants. However, such compounds are employed for the manufacture of many industrial and consumer products, hence their substitution is not possible in the near future. Suitable technologies for PFCs environmentally sound management are necessary. High energy ball milling with KOH has been proved to obtain PFCs safe destruction, but with excessive reagent. In the present study, a Waste-to-Materials solution is proposed: PFCs are co-milled with stoichiometric amounts of La_2O_3 and thus are fully converted into LaOF , a noteworthy luminescent material with many potential industrial applications. Reaction mechanism is also investigated: Ball milling process activates La_2O_3 ; this latter provokes oxidation to CO_2 and carbonization of PFCs; fluorides are incorporated into the La_2O_3 's lattice to form the oxyfluoride. Interestingly, kinetic analysis suggests that the mechanical activation of La_2O_3 might follow a zeroth-order reaction rate.

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1. Introduction

Perfluorinated chemicals (PFCs) are a large variety of manufactured organic molecules with a perfluorinated moiety (often an

alkyl linear chain). The high energy of C–F bond (533 kJ/mol, compared to C–H 473 kJ/mol, C–Cl 407 kJ/mol, and C–Br 346 kJ/mol [1]) confers to PFCs peculiar properties such as great molecular stability, tensoactivity, and insolubility in polar and non-polar solvents. Consequently, these chemicals have been extensively employed for decades in many industrial and consumer products as flame retardants, surfactants, lubricants, and coating agents

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[2–4]. Two well-known representative PFCs are perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). PFOS has been recognized to be a persistent organic pollutant (POP), because evidences for persistence into the environment [5], bioaccumulation in living tissues [6], toxicity [7,8] and long-range transport exist. In 2009, PFOS was included in the POPs list of the Stockholm Convention, while PFOA is at present under review [9].

PFCs are the emerging POPs of major concern because they are resistant to almost all destruction technologies available on the market, included advanced oxidation processes or biodegradation [5,10]. Novel technologies such as sonochemical, photochemical, γ -irradiative, subcritical, or electrochemical treatments can achieve PFOS and PFOA decomposition in aqueous solutions [10–14]. However, all these studies demonstrate that PFCs destruction necessitates of harsh conditions to obtain a significant but partial removal. In addition, they focus on aqueous system, but very little is done to propose valid alternatives for safe disposal of PFC-containing solid waste. Nonetheless, this is a serious problem because such waste, e.g. perfluorinated polymer waste, contaminated soils, PFCs stockpiles, etc., can be a secondary source of water contamination [15,16]. Currently, high temperature incineration is still the sole disposal option for such kind of waste materials. But its major problem is the production of significant amounts of corrosive HF, as well as of quite relevant quantities of CF_4 , a potent ozone-depleting gas [17]. Additional concern is solicited by possible formation of fluorinated dioxins [18]. Consequently, new technologies, alternative to thermal treatments, are highly required.

High energy ball milling (HEBM) is an emerging solvent-free technology that takes advantage of the mechanochemical (MC) activation of solids [19]. It has been successfully applied to the destruction of a large number of chlorinated and some brominated POPs [20]. Pollutants are treated with one or more co-milling reagents, providing, through countless hits of milling balls, the required energy to carry out the destruction reaction. Insertion of mechanical energy at environmental temperature and pressure causes pollutant mineralization to halides and carbon. It is demonstrated that the reaction conversion is mainly governed by the amount of mechanical energy inserted into the powder reagents, often referred to as “energy dose” [21–23]. Concerning PFCs, knowledge on their MC degradation is still poor, although few related articles have been published. In an early work, Shintani et al. [24] observed PFOS and PFOA abatement after several hours of intensive milling (i.e. 700 rpm rotation speed) with CaO in excess. However, formation of inorganic fluorides could not be detected, suggesting that CaO cannot assure the complete mineralization of PFCs. Later, our workgroup tried a different co-milling reagent, namely KOH, purposely chosen to generate soluble fluorides and to be effective also with a moderate milling intensity (i.e. 275 rpm rotation speed) [25]. Actually, PFOS and PFOA were destroyed in rapid manner (4 h), and stoichiometric fluoride recovery confirmed their entire mineralization. Nevertheless, KOH was used in excess and the final residue could not be classified as a non-hazardous waste due to its high pH value. This methodology is not sustainable yet.

In two more recent works, a Waste-to-Materials approach for MC destruction of brominated POPs was proposed by us [26,27]. It was developed to achieve the beneficial re-use of halogen content in POP molecules to form inorganic products with valuable properties. Brominated POPs were employed as bromine source and co-milled with stoichiometric amounts of Bi_2O_3 or La_2O_3 . Thus, bismuth or lanthanum oxybromides were obtained, which are compounds with peculiar catalytic and electrical properties [28,29]. Still, an intriguing aspect emerged in clear manner: Significant amounts of carbon dioxide and amorphous carbon were detected as products of MC destruction, denoting coexistence of an oxidative reaction (to CO_2) with a reductive one (to C). Carbon

formation has been extensively reported in literature, and CO_2 or carbonate formation has been observed in a considerable number of works [20]. Yet, to the best of our knowledge, concomitance of both degradation pathways has been never explained.

In the present study, several PFCs are chosen as model pollutants to investigate their MC destruction with La_2O_3 . The product of interest of the solid state reaction is nano-sized LaOF, which is an excellent host for doping with lanthanide elements because of its chemical stability and low-phonon energy [30]. Doped LaOF is known for its excellent luminescent properties and can be utilized for the manufacture of transparent oxy-fluoride glass-ceramics, which are materials with a wide range of potential applications [31]. We decided to perform the present study on the basis of several reasons.

First, it is reasonable to predict that PFCs will be amply utilized in the next 30–40 years because now their particular properties given by the C–F bond cannot be substituted by any another class of compounds, even more so at industrial scale [2]. Therefore, a green and sustainable technology for solid PFCs’ end-of-life is necessary, in order to prevent their diffusion into the environment. Although the effectiveness of perfluorinated polymer MC destruction was demonstrated with polytetrafluoroethylene (Teflon[®]) [32], specific information on PFCs destruction (i.e. reaction kinetic, degradation mechanism, by-products, etc.) is necessary for possible full-scale application. In fact, the presence of a polar group and heteroatoms radically changes the physicochemical properties of these perfluorinated molecules, compared to the polymer.

Second, preliminary economic evaluation suggests that, despite HEBM is an energivorous technology, it is still a cheap alternative to current industrial thermal process for oxyhalides production, also in nano-crystalline form [26,32–34]. Following the Waste-to-Materials approach, here we verify that PFCs can be used as fluoride donors to achieve an analogue nano-crystalline product with high purity.

Third, PFCs have typical surfactant structure and their MC destruction is carried out with stoichiometric amounts of reagents. Thus, the simplicity of the alkyl structure and the quantitative formation of the products provide clearer information on chemical and mechanochemical phenomena (compared to the MC destruction of Teflon[®] or other POPs). Specifically, we propose a possible explanation for the coexistence of a reduction and an oxidation pathway during HEBM. More importantly, kinetic analysis of the reaction suggests that MC activation of the inorganic co-milling reagent may follow a zeroth-order kinetic, which, to the best of our knowledge, was never reported for dry milling of oxides and contributes to the understanding of this fundamental MC phenomenon.

For the sake of brevity, this article presents and discusses mainly the results on PFOS and PFOA, utilizing specific outcomes obtained with other PFCs to provide further insight on reaction mechanism and kinetics. Detailed information on the other compounds is given in the [Supplementary Information \(SI\)](#).

2. Materials and methods

2.1. Materials

Potassium salt of perfluorooctane sulfonate (PFOS, CAS No. 1763-23-1, Fig. 1a, >98%, Sigma-Aldrich Co, USA), perfluorooctanoic acid (PFOA, CAS No. 68141-02-6, Fig. 1b, >98%, J&K Chemical China Ltd, China), perfluorohexane sulfonate potassium salt (PFHxS, CAS No. 3871-99-6, Fig. 1c, >98%, Wuhan Silworld Chemical Ltd, China), perfluorobutane sulfonate potassium salt (PFBS, CAS No. 29420-49-3, Fig. 1d, >98%, Wuhan Silworld Chemical Ltd, China), perfluoroalkoxybenzene sulfonate sodium salt (OBS, a sur-

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