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MECHANOCHEMICAL DESTRUCTION OF POPS FOR USEFUL OXYHALIDES PRODUCTION: A WASTE-TO-MATERIALS APPROACH

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Introduction

The first twelve pollutants included in the Stockholm Convention's POPs list were all chlorinated compounds. However in the last decade brominated and fluorinated pollutants have attracted increasing concern due to accumulation of evidences about their toxicity and persistency in the environment. In fact, some of these compounds were classified as POPs and included in the list, specifically: per#uorooctane sulfonate (PFOS), per#uorooctanoic acid (PFOA), polybromodiphenyl ethers, and hexabromocyclododecane (HBCDD).

Even if a global inventory of such chemicals has not been compiled yet, it is reasonable to suppose that large amounts of brominated and fluorinated POPs are stored in the world. On one hand, their safe and adequate disposal, i.e. their mineralization, is necessary, but on the other hand it represents an economic burden that governments are hardly willing to face. Moreover, the sole destruction cannot take advantage of halogens content in POPs, although such elements are valuable for industry. The halogens recovery to produce useful materials would make POPs destruction a profitable business.

Mechanochemical destruction (MCD) is an emerging technology that in the last two decades has been amply proved to be effective for POPs mineralization. It is realized at room temperature and without solvents by high energy mills that provide the mechanical energy required for the destruction. Utilizing opportune co-milling reagents, halogenated organic pollutants are converted to halides and amorphous carbon within few hours of treatment (1).

In the present work, it is demonstrated how this technology can be used not only to destroy fluorinated and brominated POPs, but also to recycle valuable elements, implementing a waste-to-materials approach. MCD of POPs produces useful lanthanum oxyhalides, which are interesting materials with unique luminescent, catalytic and electric properties (2). Specifically, LaOBr is utilized as X-ray radiographic receptor in intensifying screens for medical imaging, while LaOF can be used for the production of special oxy-fluoride glass-ceramics. Therefore MCD might be employed as a cheap route for metal oxyhalides synthesis, alternative to the energy-consuming direct solid state reaction between metal oxides and halides at high temperature (~1200°C). In this way brominated and fluorinated POPs can be beneficially converted in environmentally sound manner into inorganic products with high added value.

Materials and methods

Lanthanum (III) oxide was employed as co-milling reagent. MCD of PFOS (potassium salt), PFOA, decabromodiphenyl ether (decaBDE), and HBCDD was realized employing two planetary ball mills, using opportune operating parameters. The powder mixture was composed of 3 g of reagents (viz. La_2O_3 and one POP, using an atomic ratio La:X=1, where X=F, Br), which were loaded into zirconia jars with zirconia balls. Milling tests were repeated for various durations, until completion of the reactions, i.e. product formation and POPs destruction.

Fluorinated pollutants in milled samples were extracted by 30 min ultrasonic treatment in 50 mL methanol and analyzed by HPLC with a conductivity detector; samples with brominated POPs underwent extraction with hexane:acetone 1:1 by the same procedure and were quantified by GC-MS. Inorganic phase products were identified by X-ray diffraction (XRD) and thermogravimetric analysis (TGA). Changes in POPs chemical structure during milling were assessed by Fourier transform infrared (FTIR) spectroscopy with the KBr disk method and by Raman spectroscopy.

Results and discussion

POP destruction rates and inorganic products

The destruction of fluorinated and brominated POPs is achieved in safe and effective manner after the high energy ball milling (fig. 1a). POP destruction percentages higher than 95% are obtained at the end of the treatment. However, different reaction rates are observed. In particular, perfluorinated compounds seems to undergo a facile destruction that requires low mechanical energy amount provided by balls hits (i.e. ~5 kJ/mg, which correspond to 8 h milling at 300 rpm rotation speed), while brominated POPs necessitate of high energy input to be destroyed (i.e. ~17 kJ/mg for decaBDE and ~35 kJ/mg for HBCDD, which are provided by 4 and 8 h milling, respectively, with a rotation speed of 700 rpm). Such difference in destructibility among pollutants is explained by the presence of weak bonds in the molecules. Specifically, the bond between the acid group and the perfluorinated chain is easily broken under low energy milling; the oxygen bridge in decaBDE is the most probable point of rupture but is more stable than the above-mentioned bond in perfluorinated POPs, while the cycloalkane ring of HBCDD require higher energy dose to be broken under mechanical action.

Fig.1 – MCD trends of POPs (a) and the corresponding oxyhalides formation (b) under high energy ball milling (reaction progress is expressed in term of cumulative mechanical energy provided to the reaction mixture, i.e. the energy dose).

Nevertheless, POP molecules are completely dehalogenated to form inorganic oxyhalide, thus ensuring that unintentional POPs generation during the MCD treatment is averted. In fact, formation of oxyfluoride from the perfluorinated pollutants and of oxybromide from the brominated flame retardants is proved by XRD analysis. Rietveld fitting of diffractograms allows the quantifications of La_2O_3 and LaOX during the reaction, confirming the stoichiometric conversion of the oxide (fig. 1b). POPs dehalogenation provoked by MCD produces halides that are more or less promptly incorporated into the La_2O_3 lattice and substitute the oxide centers to form oxyhalide. Milled samples were extracted by water to recovery halides, but very low concentrations were detected, corresponding to less than 5% of the total amount. This corroborates the rapid incorporation of halides into the La_2O_3 lattice to form LaOX.
TGA was carried out under N_2 flow to detect the thermal degradation of residual POPs and their organic by-products. Weight losses are compatible with POPs concentration in fig. 1a, suggesting that, once the molecule is fragmented by mechanical forces, it is rather quickly dehalogenated and destroyed. Thermograms highlight also the presence of carbonate, which is decomposed above 450°C. This suggests that CO_2 is a product of the POPs destruction and that it is captured by La_2O_3 to form carbonate. It is known that lanthanum compounds have a remarkable affinity for CO_2 and rapidly adsorb such gas under ball milling conditions (3).

Fig.2 – Raman spectra of powder residue after milling

Molecular transformations of POPs

In order to ascertain the complete destruction of POPs into a non-hazardous material, Raman and FT-IR spectrometric analysis were carried out on milled samples. Raman spectra of POPs after high energy milling (fig. 2) show the presence of two bands, called "D-band" (1330–1380 cm^{-1}) and "G-band" (1540–1580 cm^{-1}), which are attributed to the presence of carbon. In particular, D-band is ascribed to sp^2-bonded carbon with a disordered (i.e. amorphous) structure, while G-band is originated by graphite. After POPs dehalogenation through radical mechanism, the carbon atoms firstly form the stable aromatic rings, generating, then, a graphitic structure; secondly, further intensive milling destroys the ordered structure producing amorphous carbon. FT-IR analysis corroborates the complete destruction of organic pollutants, since all signals ascribed to structure vibrations of POPs (in particular, the peaks related to carbon-halogen bonds) are not observed in spectra of their corresponding milled residues. In addition, FT-IR confirms the presence of carbonates in the products.
The carbonization of the four POPs' entire carbon structure guarantees that the milled residue is a non-hazardous material. It is worth reminding that stoichiometric ratios were used to prepare the reaction mixture: Under such conditions, complete destruction of pollutants (with other co-milling reagents) was very rarely achieved by high energy milling (1).

Beneficial use of the MCD product

The final products have specific interest for industrial applications. However, the presence of carbonaceous matter represents an impurity in the produced material, but mild temperature calcination under air can remove such secondary product, assuring the oxyhalide purification. In particular, the residue deriving from MCD of perfluorinated POPs can be profitably utilized to prepare special glass-ceramics, which are composite materials with nano-crystalline phase into a glass matrix that can be prepared by melting of glass-ceramic precursors. The melting process assures the removal of the carbonaceous matter.

Glass-ceramics are of great interest because small quantities of lanthanides can be used to dope the crystalline phase to enhance optical activity (e.g. luminescence) of the whole glass composite. In general, LaF_3 is employed to generate such nano-crystals into the glass phase, but LaOF is recognized to be a better host for doping because of its chemical stability and low-phonon energy (4). However, due to the very expensive production process, LaOF is hardly considered an economically viable precursor for the preparation of doped glass-ceramics. We carried out preliminary tests with the milled residue to assess its usability as component in oxy-fluoride glass-ceramics. Differential scanning calorimetry outcome confirms that LaOF crystallites can be formed in the glass phase and that any carbon impurity deriving from POPs MCD is oxidized to CO_2 during heating. Hence the MCD residue can be employed as-produced.

In conclusion, the MCD of fluorinated and brominated POPs with La_2O_3 was realized following a waste-to-materials approach, achieving two important effects: the safe disposal of toxic hazardous waste and the stoichiometric production of a residue that can be used for the manufacturing of high added value materials. In this way, the disposal of the huge amounts of such obsolete POPs can be considered an economically convenient business, thus giving a potent stimulus to their environmentally sound management.

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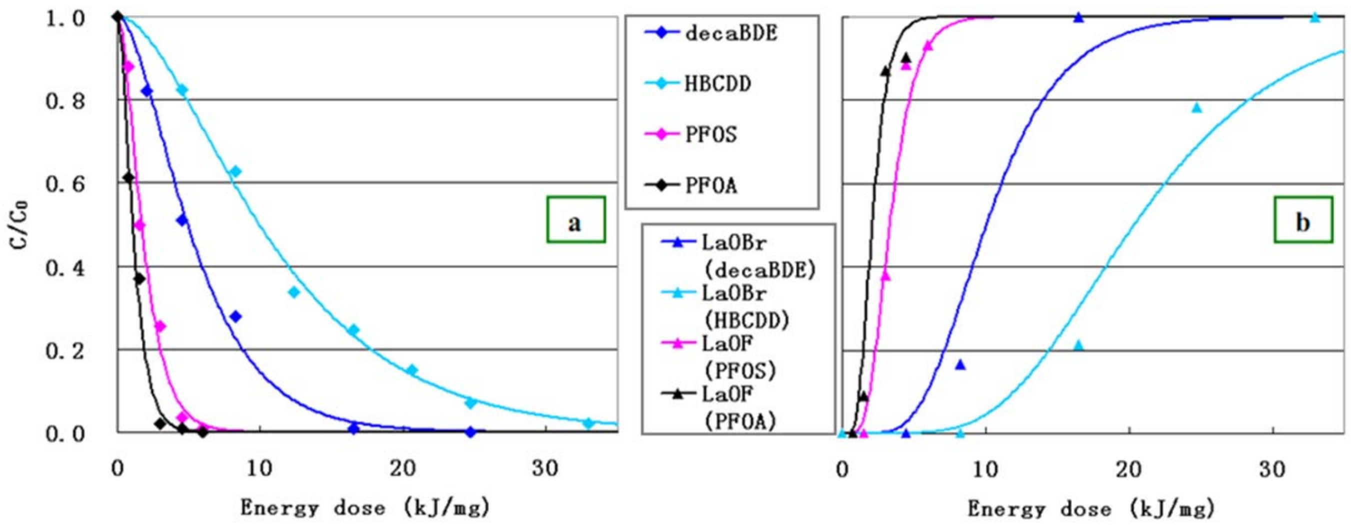

Figure 1

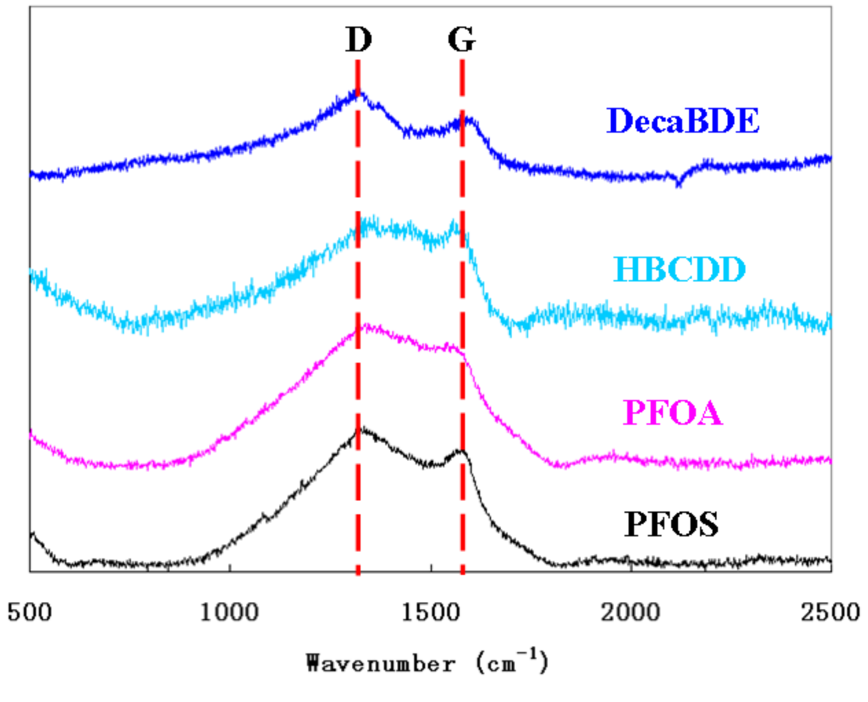

Figure 2