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Research paper

Mechanochemistry: A review of surface reactions and environmental applications

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ABSTRACT

Mechanochemistry is the study of physico-chemical transformations generated by mechanical force. This force may break down crystals, thus exposing fresh, active surfaces and enhance the mass transfer required for reaction partners in the solid state to make the contact required for initiating a chemical reaction. Application of mechanical force may facilitate sorption-induced steric enhancement of transformations catalyzed by ions of transition metals (e.g., cations of such metals serving as counter ions in exchange complexes of clays). The formation of mixed Cu–Na–montmorillonite from Na–montmorillonite ground with $CuCl_2$ in the presence of imazaquin and the resultant breakdown of imazaquin is one example of this phenomenon. Reported mechanochemical reactions which involve minerals, include redox reactions, polymerization and polymer rearrangements, recrystallization and dehydration. The more widespread methods for removing organic contaminants from soils are based on biological degradation. Biological processes, however, have certain shortcomings such as the substantial time they require, or the significant concentrations of harmful residues that are left in the soil. Alternative soil remediation schemes are, therefore, needed and mechanochemical procedures may be part of such innovative cleanup protocols. Mechanochemistry can be applied at the field scale and mechanochemical techniques were already suggested as a clean and cheap approach to hazardous waste management and destruction. Furthermore, soil tillage is actually a process in which mechanical force is applied to the soil and hence, it may induce a variety of mechanochemical reactions.

Clays and metal (especially iron and manganese) oxides catalyze numerous transformations of organic compounds when such compounds are sorbed on the minerals' surfaces. The catalytic efficiency of these minerals is, at least in part, due to their strong acidity, both Bronsted and Lewis, and to the large specific surface area they may possess. Manganese and iron are redox active and their minerals are thus capable of supporting both electron and proton transfer reactions. Since iron oxides are abundant in soils, transformations augmented by these minerals are of considerable environmental importance. In the present review, case studies of mechanochemically induced transformations of pollutants are presented. The breakdown of pesticides (2,4-D, imazaquin and atrazine) and of other organic pollutants such as DCP and PAHs achieved by light grinding for short durations (a few minutes) in a mixture with minerals which are soil components or the derivatives of such components is described. Among the tested minerals, Al– and Cu–montmorillonite, iron oxides and Mn oxides were the most effective heterogeneous catalysts. The effectiveness of the minerals depended strongly on the degraded pollutant and on the conditions (e.g., the moisture content) under which the mechanochemical reaction took place. Although the presence of water often hinders the degradation, in some cases the reverse is true. Na–montmorillonite in the presence of $CuCl_2$ was effective in degrading imazaquin when the mixture was ground wet. This demonstrates a detoxification process applicable to real-world systems which are often wet.

1. Introduction

Mechanochemistry is a branch of science that deals with physico-chemical and chemical transformations induced by mechanical force. Such a force (e.g., as applied by grinding) may perturb the crystal structure of solids (thus exposing or creating fresh surfaces rich in active catalytic sites), and provide the driving force for the mass transfer required for bringing into contact reactants of solid state chemical reactions. Pressure or shear stress applied to impacted particles may facilitate both unique phase transitions and chemical transformations. The enhancement of catalytic capacity upon grinding may be in many cases due to the supply by mechanical means of the energy required to break bonds in the solid medium, thus exposing fresh surfaces, rich in unstable sites (the partner atoms in the broken bonds) to the substrate molecules. The mechanical agitation may also help orient the sorbed molecules relative to the newly formed, catalytically efficient sites, at the optimal conformation for the surface reaction to occur (Beyer and Clausen-Schaumann, 2005;

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Hall et al., 1996; Loiselle et al., 1997; Mingelgrin et al., 1978; Nasser et al., 2000; Pizzigallo et al., 2004; Shin et al., 2000; Tanaka et al., 2005).

Reported mechanochemical solid state reactions include a wide range of processes, such as oxidation-reduction, polymerization and polymer rearrangement, recrystallization and dehydration (e.g., Balaz et al., 2005; Filipovic-Petrovic et al., 2002; Harchova et al., 2007; Kalinkin et al., 2006; Mendelvici, 2001). Mechanochemical techniques were used to manipulate the mode of adsorption of organic substances on clay minerals (Landau et al., 2002) and were suggested as an easy, clean and cheap novel approach to polluted soils and hazardous waste management and destruction (Brike et al., 2004; Caschili et al., 2006; Hall et al., 1996; Loiselle et al., 1997; Montinaro et al., 2007; Napola et al., 2006; Nasser et al., 2000; Pizzigallo et al., 2004; Shin et al., 2000; Tanaka et al., 2005). Mechanochemistry can be applied relatively easily at the field scale for remediation of polluted soils (e.g. http://www.tribochem.de, 2002). Furthermore, soil tillage practices such as plowing, or disking are actually processes in which a mechanical force is applied to soil particles and hence, soil tillage may initiate a variety of mechanochemically induced reactions.

Clay minerals and certain metal (e.g., iron and manganese) oxides are major contributors to the catalysis of abiotic transformations of organic pollutants in natural environments (e.g., Nzengung et al., 2001; Wolfe et al., 1990). Clays may constitute half or more of the solid fraction of soils and are known to catalyze numerous transformations of organic compounds when those are sorbed on their surfaces (e. g., Mingelgrin et al., 1977; Nasser et al., 1997; Wang and Huang, 2003; Weiss et al., 2002; Wolfe et al., 1990). The catalytic efficiency of clay minerals and metal oxides is attributed in many cases to their capacity to function as strong acids, both Bronsted and Lewis, and to the large specific surface area they often possess (especially expandable clays). Manganese dioxides, for example, have highly acidic surfaces due to the interaction upon hydration of terminal hydroxyl groups and of bridging oxygen atoms with water molecules. Like manganese, iron is redox active and is capable of supporting both electron and proton transfer reactions. Since iron oxides are abundant in soils, transformations enhanced by these minerals are environmentally important.

It is reasonable to assume that application of mechanical force will facilitate sorption-induced steric enhancement of many transformations catalyzed by transition metals, for example by cations of such metals serving as counter ions in exchange complexes of clays. The potential role of exchangeable copper in enhancing mechanochemical degradation is demonstrated below for imazaquin.

Mechanochemistry does not only deal with enhanced catalysis. Applying mechanical force may induce, for example, the formation of solid phases which are of environmental importance or otherwise of interest. Yariv et al. (1991, 1994) reported the formation of kaolinite intercalated with alkali halides (CsCl and CsBr) by mechanical force (grinding). Yariv and Lapides (2000) described mechanochemical phenomena occurring during grinding of kaolinite. Kaolinite was ground in the absence as well as in the presence of alkali halides and using IR spectroscopy, those authors demonstrated the occurrence of four types of mechanochemical effects: diffusion of atoms (mainly protons, "prototropy"), delamination, layer breakdown, and adsorption of atmospheric water by the amorphous grinding product. When the smectites montmorillonite, beidellite, saponite, and Laponite were ground with excess phenol (ibid.), in most cases the first 5 min of grinding led to an increase in the adsorption of the phenol while additional grinding resulted in a decrease in phenol adsorption. Given below (imazaquin section) is an example of the formation of Cu–montmorillonite from Na–montmorillonite ground with $CuCl_2$ and the enhancement of the degradation of imazaquin by this transformation.

The overall objective of this review is to present case studies of mechanochemically induced transformations of pollutants, including pesticides (e.g., atrazine, 2,4-D and imazaquin) and other organic substances such as 2,4-dichlorophenol (DCP) or polycyclic aromatic hydrocarbons (PAHs), using light grinding for short durations (on the order of minutes) in a mixture with minerals. The investigated pollutants and their structural formulae are presented in Appendix 1. The minerals used were soil components or derivatives of such components, specifically clays and metal oxides.

2. 2,4-D and DCP

The role of manganese oxides in promoting oxidation of organic compounds is well documented (e.g., Cheney et al., 1996) and accordingly, a number of the mechanochemical reactions described in the present review involve such oxides. Birnessite was ground manually with wide range of pollutants: 2,4-D (Nasser et al., 2000), atrazine (Shin et al., 2000) organo-clorinated compounds (Pizzigallo et al., 2004) and imazaquin (Nasser et al., 2009). Excluding imazaquin, the other mentioned compounds degraded in a matter of hours at ambient temperature on the surface of birnessite.

The mechanochemical degradation of the widely used herbicide 2,4-D (2,4-dichlorophenoxyacetic acid; the molecular structure is presented in Appendix 1) on synthetic birnessite (δ-MnO_2) was investigated by Nasser et al. (2000). The authors used light grinding (5 min in an agate mortar -O.D 100 mm- and pestle). The apparent activation energy, evaluated by heat conduction calorimetry, was estimated to be 37 kJ mol^{-1}. Two degradation products were identified, 2,4-dichlorophenol (DCP), and CO_2. No consumption of gaseous oxygen was detected, but some Mn(IV) of the birnessite was reduced Mn(II). A positive correlation was observed between the amount of Mn(II) produced and CO_2 evolved, suggesting that the decomposition of 2,4-D involved the Mn oxide, birnessite, as a source of oxygen and Mn(IV) as an electron acceptor.

The mechanochemical degradation of 2,4-D on birnessite is summarized in Fig. 1. Nasser et al. (2000) reported that, DCP, the primary degradation product of 2,4-D, further degrades on the surface of birnessite. Hence, the present authors undertook to study the effect of applying mechanical force on the fate of DCP in the presence of birnessite as well as other solid phases. Aside from birnessite, hematite (α-Fe_2O_3) and Na– and Cu–montmorillonite were tested as solid phases.

DCP (its molecular structure is presented in Appendix 1) is one of the most important chlorophenols used in the manufacture of pesticides. It is the key-intermediate in the synthesis of 2,4-D. DCP is also a major feedstock in the production of certain compounds used in mothproofing, antiseptics and seed disinfectants (Bauer et al., 1999; Kroschwitz, 1993; USEPA, 1980). Thus, chlorophenol is considered as an EPA priority pollutant and it was detected in hazardous waste sites, wastewater and drinking water (ATSDR, 1995; Laurenti

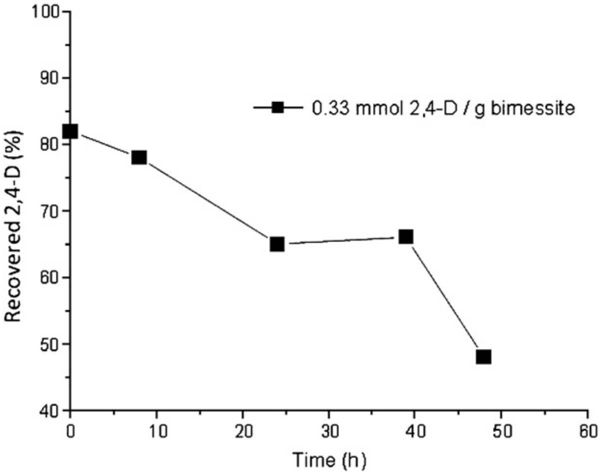

Fig. 1. Kinetics of 2,4-D disappearance after grinding for 5 min in the presence of birnessite (adapted from Nasser et al., 2000).