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Analyses of Mechanochemical Reactions at the Boundary between Metal Oxide – Organic Fine Particles and Their Practical Application

M. SENNA

Faculty of Science and Technology,
Keio University, 3-14-1, Hiyoshi, Yokohama 223-8522 (Japan)

E-mail: senna@applc.keio.ac.jp

Abstract

Starting from the colour change upon co-milling a white mixture comprising a metal oxide (MO) and organic solids (OS) with F or N, general features of the mechanochemical reactions at the boundaries between MO and OS were observed, characterized and discussed with the presence of various analytical results. Three parallel streams of the mechanochemical reactions upon co-milling are confirmed, *i. e.*, i) an oxidative decomposition of the organic species, ii) formation of nanostructured carbon, and iii) incorporation of non-oxygen anionic species into oxides via a ligand exchange. In the case of wet milling, complex ion formation in a liquid phase is sandwiched. Case studies were focused on TiO₂ as MO and polytetrafluoroethylene (PTFE) or glycine (Gly) as OS.

Key words: metal oxides, TiO₂, PTFE, glycine, ligand exchange

INTRODUCTION

One of the recent remarkable trends of the mechanochemical community is an increasing stream into materials science, as delineated in a recent comprehensive review [1]. The area is also extended to organic chemistry [2]. Mechanochemical interaction between inorganic and organic materials, on the other hand, has been studied much less in extent [3], namely in rather restricted areas, *e.g.* in pharmaceuticals [4, 5] or in environmental sciences for the decomposition of hazardous materials [6, 7]. Elucidation of these processes from various physicochemical viewpoints would lead us to a new kind of surface modification and functionalization of various metal oxides. A particular charm of the mechanochemical phenomena at the boundary of metal oxides (MO) and organic solids (OS) is the combination and synergy, among different phenomena occurring at the boundary of the both parties, as the author recently reported [8–10].

In the present short review, the author tries to reply to the question, what happens by co-

milling MO nanoparticles with powdered OS, mainly by featuring his recent research works. The purpose is to close up some particularities at the boundaries, by taking 3 case studies made by the author with various co-workers, *i.e.*, fluorination of TiO₂ with polytetrafluoroethylene (PTFE) [8, 9], and nitridation of TiO₂ with glycine and antibacterial photocatalysis [10].

INCREASED LIGAND FIELD STRENGTH AND REACTIVITY BY SYMMETRY LOSS

Construction units of most of the MOs are either MO₄ tetrahedra or MO₆ octahedra. Incorporation of non-oxygen anions into these metal oxides is, therefore, regarded as a ligand exchange of one or more oxygen atom(s) in MO. On the other hand, a ligand field strength, seemingly specific to the central metallic species, changes with the state of the polyhedra, mostly *via* a symmetry change. Symmetry loss takes place *via* i) macroscopic crystalline deformation, and ii) loss of some of the oxygen at-

oms from the polyhedra. The case i) is a result of inelastic deformation of the crystalline materials under mechanical stress. This is applicable even to the brittle materials when we observe microscopic local spaces or fine particles, due to microplasticity (MP) [3, 11–13]. The case ii) is a popular chemical process under various conditions, including heating under a reducing atmosphere. Interplay between i) and ii) also occurs frequently, particularly in the solid state systems under mechanical stressing. A reaction-induced amorphization under mechanical stressing is an example [14, 15].

Decrease in the polyhedral symmetry and associated change in the electronic states were studied in depth for well defined substances, notably with single crystals [16, 17]. In the case of mechanochemical phenomena, in contrast, these phenomena are much more complicated, due primarily to the inhomogeneous and diverse states of the metal–oxygen polyhedra. This makes us difficult to examine these issues of polyhedral symmetry by X-ray diffractometry, however exact we try to refine the results, *e. g.* by advanced Rietveld refinement. We, therefore, need some other analytical tools, among others different spectroscopic analyses [18].

A brief review on the mechanochemical changes on the coordination compounds will be helpful to understand the main issues to be mentioned in the next section. This is implemental for two reasons, *i. e.* i) their crystalline states are regarded as molecular crystals, to which organic crystals are generally belonging, and ii) building units of transition metal coordination compounds have the units of ML_6 octahedra or ML_4 tetrahedra, within which dative bonds are predominating between M and the ligand (L). These M–L dative bonds predominate most of the metal coordinate compounds, irrespective of the ligand species. This is isomorphous with the MO_6 octahedra or MO_4 tetrahedra in most of the metal oxides.

The MO_6 or ML_6 octahedra possess 4-fold symmetry, ideally with O_h octahedral symmetry, within which dative bonds are predominating between M and O or L, in a same manner of those in the coordination compounds. The degree of symmetry is reduced when they are distorted. Deletion of one or several oxygen atom(s) or ligand(s), breaks symmetry and

destabilizes the polyhedra. In other words, the reactivity of such polyhedra is inevitably elevated, to ease any of the solid state reactions involving such a coordination compound. As we have examined mechanochemical synthesis of a series of pyridyl coordination compounds, *e. g.* by starting from the mixture of $FeCl_2 \cdot 4H_2O$ and bipyridine or 1,10-phenanthroline [15]. This is a simple example of the ligand exchange between oxygen of a ligand, H_2O with nitrogen of those pyridyl compounds, under mechanical stressing.

MULTIPLE CHEMICAL PROCESSES AT THE BOUNDARY BETWEEN MO AND OS

Some of the consequences of milling a mixture, such as mechanical alloying or direct mechanochemical synthesis of inorganic materials are already established. The main issue involved is a mechanical diffusion [19]. Mechanochemical phenomena at the boundary or the contact points among MO and OS particles are much more complicated [16, 17]. Bonding states in MO are known to be more or less ionic, in contrast to those in OS, which are intermolecular to form a molecular crystal. When OS has a contact with MO, surface oxygen will serve as a nucleophilic species to preferentially attack the electrophilic part of the OS surface.

A scheme given in Fig. 1 symbolizes the entire phenomena, when we co-mill TiO_2 with PTFE. The first remark is the darkening of the mixture from white to black. This is primarily

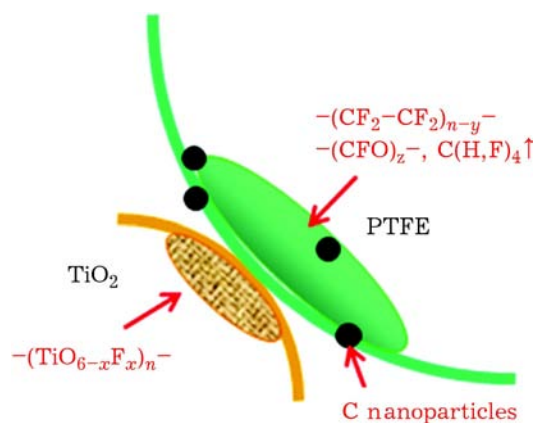


Fig. 1. Scheme of the mechanochemical reaction at the contact point between TiO_2 and PTFE.

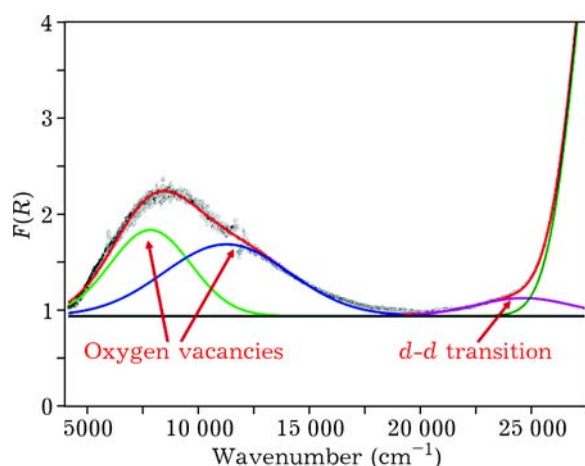


Fig. 2. Diffuse reflectance spectrum of the mixture of TiO_2 and PTFE after co-milling for 3 h.

attributed to the introduction of oxygen vacancies into the oxide part, implemented by the unique absorption in the visible and near infrared region (Fig. 2). It is well known that the introduced vacancies serve as a colour centre [20, 21]. A mechanochemical reaction at the particle boundary is also visible under electron microscope. As shown in Fig. 3, severe agglomeration and near surface amorphization take place simultaneously after co-milling.

Incorporation of fluorine into titania is verified unambiguously by the change in the $\text{F}1s$ XPS peaks, as shown in Fig. 4. When PTFE was milled without MO, the $\text{F}1s$ XPS spectrum is peaked at around 690 eV, as shown in Fig. 4, A with no significant differences from that of pristine PTFE. After co-milling with TiO_2 , a new

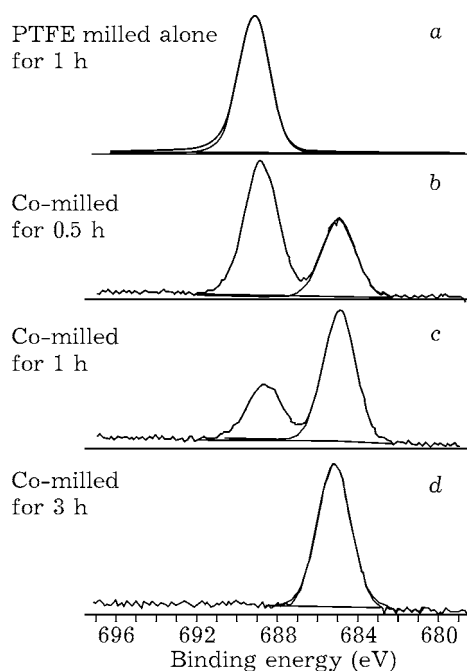


Fig. 4. $\text{F}1s$ XPS profiles of TiO_2 co-milled with PTFE for varying milling time.

$\text{F}1s$ XPS peak appeared at around 685 eV. The intensity of the latter peak increased with co-milling time, as observed from Fig. 4, b and c. The new peak is similar to the one observed from TiOF_2 [22–25]. This is a clear evidence of the transfer of fluorine from PTFE toward titania by co-milling. After prolonged milling, only the latter peak was recognized (see Fig. 4, d).

Another important observation of co-milling TiO_2 with PTFE is the formation of nanostructured carbon species. As shown in Fig. 5,

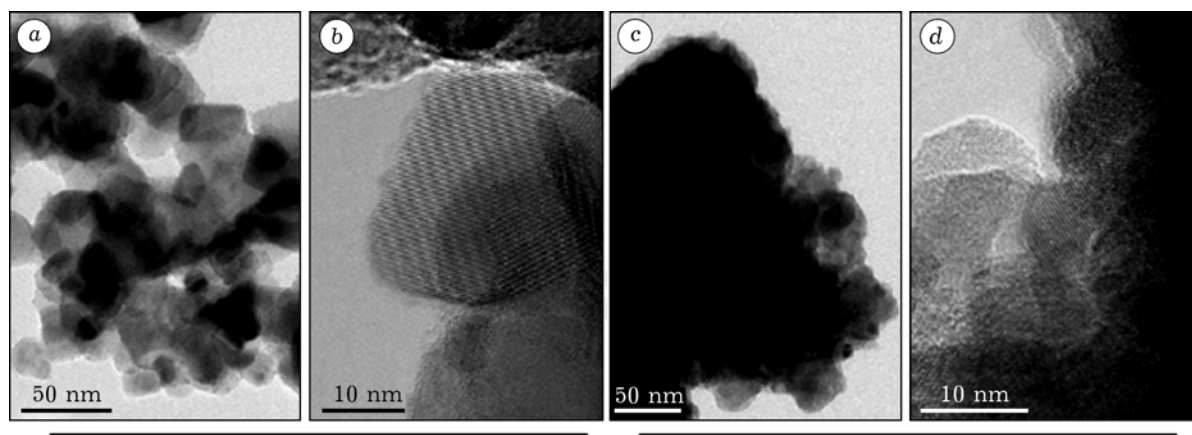


Fig. 3. Transmission electron micrographs: a, b – intact TiO_2 ; c, d – TiO_2 co-milled with 10 mass % PTFE for 3 h.

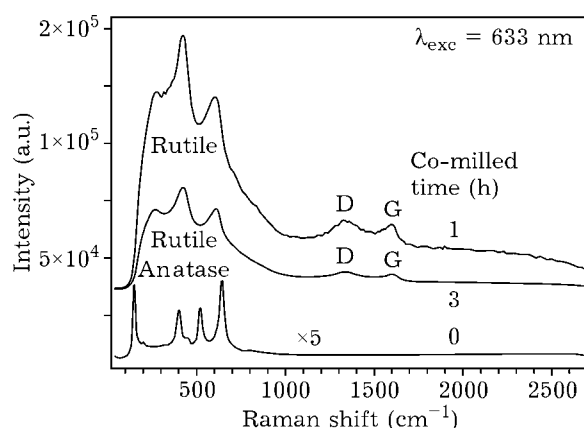


Fig. 5. Raman scattering spectra of the mixture of TiO_2 and PTFE after co-milling for varying duration.

we observe 4 strong Raman bands characteristic of anatase [26] in the initial mixture before milling. After co-milling for 1h, the Raman spectra exhibited a clear change of the lattice vibrational modes of rutile [27]. At the same time, two new bands appeared at around 1350 and 1590 cm^{-1} . They are ascribed to the D and G bands of carbon nanoparticles [28, 29].

When we observe MO as a catalyst of an organic chemical reaction, we may regard the oxygen atoms on the surface of MO as the nucleophilic agents. Therefore, when they encounter OS, the electrophilic part of the OS surface can be attacked by the surface oxygen of MO. This is the start of oxidative decomposition of OS by abstracting the oxygen from MO. What is left in the MO at this stage, is the oxygen vacancies at the surface of MO.

Unlike the “still” condition of most of the solid state reactions taking place in a furnace, a mechanochemical process associated with co-milling is always combined with mixing, so that the contact points between MO and OS are constantly renewed. On top of that, mechanical stress enables local inelastic deformation, close to the state of kneading the entire mass. Such a local deformation is understood under the concept of MP, as mentioned in the section 2 [3, 11–13]. Occurrence of MP is enhanced by the local reaction at the contact points.

Chemical states of the oxygen at the surface of MO are quite complicated. This is verified not only by the broadened spectra, but also by the colour change. Formation of nar-

row bands corresponding to the visible light photon energy is associated with the near surface bands [30], associated with the oxygen vacancies. By thoroughly examining the valence band (VB) XPS spectra of partially reduced titania nanoparticles, Naldoni *et al.* attributed the formation of narrow band gaps, responsible for the colouring of titania, to the electronic transitions from both tailed VB and oxygen vacancies' (VOs) localized states to the conduction band (CB) [30]. Thus, the colouring or darkening of titania, in conjunction with the formation of oxygen vacancies, is one of the key issues for the incorporation of anionic species *via* a mechanochemical route under the coexistence of OS.

The mechanochemical procedure given above is associated with the concept of surface modification and “near surface” region. At the same time, the volume fraction of the changes in the near surface region will become very significant when the particle size is reduced in the nanometric region. When the particle size is 100 nm and the modified near surface thickness is 5 nm, the modified volume amounts to 27 vol. %.

MECHANO-CHEMICAL REACTION AT THE SOLID–LIQUID BOUNDARY

When MO is milled in a liquid containing OS, the phenomena are slightly different. A wet processing is more intricate, but it will be more beneficial with less tendency of particle agglomeration, and easier formation of complex ionic species in the solution phase. Hydrated complex

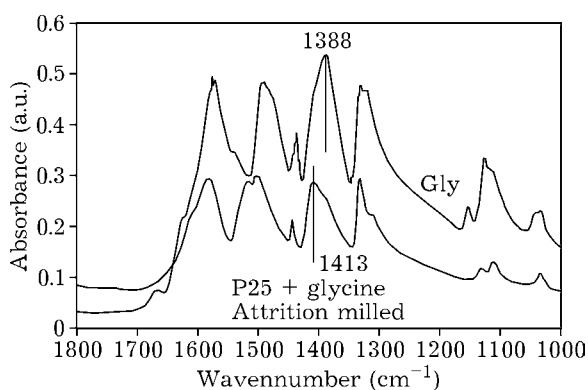


Fig. 6. FTIR spectra of Gly and the co-milled product of TiO_2 in aqua solution.

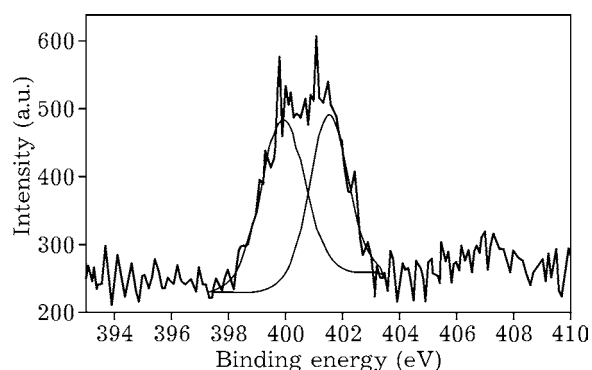


Fig. 7. N1s XPS profiles of the co-milled product of TiO_2 in aqua solution of glycine, with peak deconvolution.

species can deposit on the surface of the dispersing particles. When the product is dried, those complexes are dehydrated and decompose upon subsequent heating. Combined with such a post treatment, some anionic species like nitrogen could migrate into the interior of the oxide particles and are incorporated into the oxide lattice, to complete anion exchange.

Amino acids are water soluble, stable and relatively inexpensive. Glycine (Gly), one of the simplest and representative amino acid, was

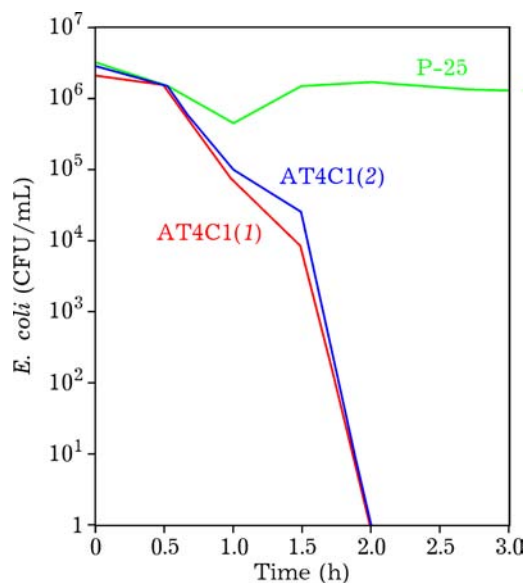


Fig. 8. Antibacterial photocatalytic activity under blue lights of titania (P-25) and the co-milled product of TiO_2 in aqua solution of glycine after annealing at 500°C in air (AT4C1) with two different batches, (1) and (2) prepared under the same condition.

dissolved to give an aqueous solution, in which titania nanoparticles were attrition milled [10]. Mechanochemical reaction on the surface of titania was demonstrated by the diffuse reflectance IR spectra. As shown in Fig. 6, we ob-

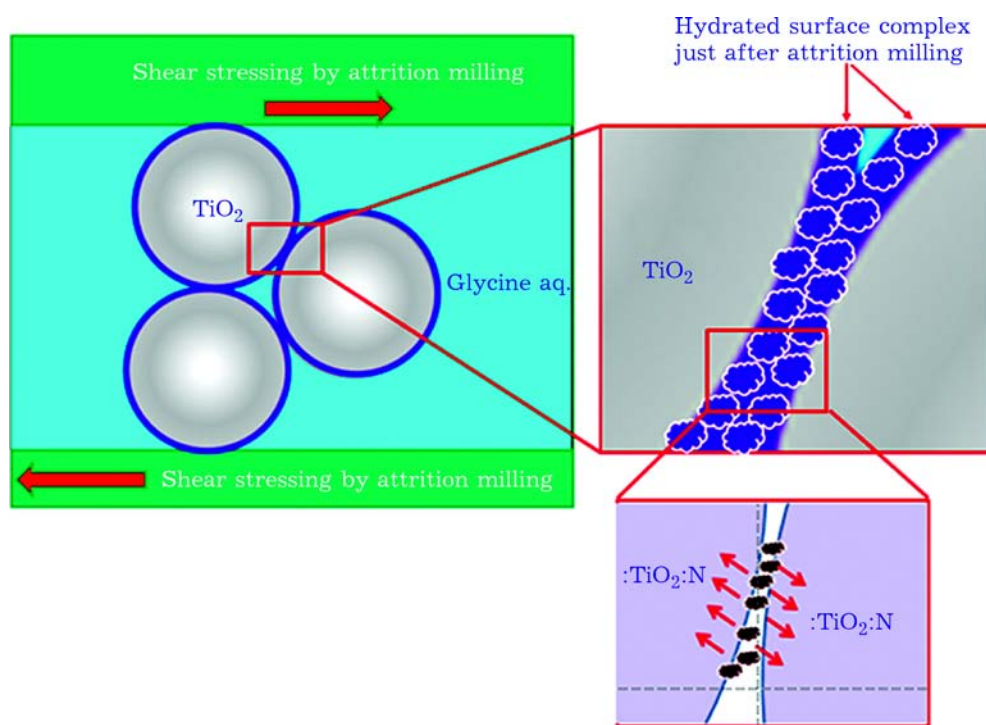


Fig. 9. Scheme of the mechanochemical reaction.

serve a clear shift of the COO^- related quartet-peaks. Bimodality of the N1s XPS profile, shown in Fig. 7, is another indication of interfacial mechanochemical reaction between titania and Gly.

After annealing the co-milled and dried sample up to 500 °C in air, the sample turned from white to pale yellow. An antiviral photocatalytic activity with model microorganisms (*E. coli*) was then examined. Figure 8 shows a drastic decrease in the *E. coli* concentration upon irradiation of a blue light. A scheme of the mechanochemical reaction is illustrated in Fig. 9. Formation of the hydrated complex in an aqueous phase, and subsequent diffusion of nitrogen into the lattice of TiO_2 are the key issues of the present preparative process of antibacterial photo catalysis [10].

CONCLUDING REMARKS AND NEAR FUTURE OUTLOOK

The present mechanochemical processes occurring at the boundary between MO and OS are quite general so that the similar phenomena are observed in the wide varieties of the MO-OS combination, *e. g.* ZnO , Nb_2O_5 or SnO_2 as MO, and glycine, polyvinylidene fluoride or urea as OS. Anion exchange and introduction of oxygen vacancies generally enhance ionic and electron conductivity and increase solar energy harvest. By selecting the condition of mechanical stressing, we may control the introduction of narrow gap bands, though the process is not at all simple.

Another remark to be made is importance of the applicability and the affordability of the cutting-edge technology to industry. Mechanochemistry has arrived at its turning point. While it made success to come out of the state of black box to have established some of the mechanisms involved in an atomic scale. Participation of a number of scientists of the genres other than the mainstream of its development, namely, mining, mineralogy and metallurgy, *e.g.* from organic chemistry, was one of the locomotives to promote this trend. However, the development in this direction requires, like many examples of nanotechnology, mechanistic study as well. We have always to keep in mind the necessity and compatibility of the upstream and downstream research studies.

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