Effective Utilization of Grinding and Mechanochemistry to Recycling and Separation

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Abstract
The authors introduce novel research results on material synthesis and recycling by grinding. The research is focused at first mechanical activation of fine particles of solid material caused by grinding, and this leads to synthesize functional material from two starting materials without heating. One of the examples is to show the formation of complex oxides such as CaTiO$_3$ from CaO and TiO$_2$. Another one is dechlorination of PVC by its grinding with CaO to form CaOHCl and hydrocarbon. This means that it is possible to separate chlorine from PVC by its washing with water. Grinding operation enables us to reduce indium (In) by from indium oxide (In$_2$O$_3$) and ITO in the presence of Li$_3$N under NH$_3$/N$_2$ gaseous environment. The reaction can be given by: In$_2$O$_3$ + Li$_3$N + NH$_3$$\rightarrow$ 2In + 3LiOH + N$_2$. The purity of In and its recover are quite high over 90%. Further example of the mechanical activation followed by heating up to about 400$^\circ$C is to generate hydrogen (H$_2$) from biomass such as wood and straw. The biomass is milled with inorganic substance such as CaO, followed by heating at non-oxidative environment. The generation of H$_2$ in high concentration can be attained during heating, due to adsorption of CO$_2$ and CO by CaO to form CaCO$_3$. This implies that the grinding plays a big role to bring out many possible applications for material synthesis, material and waste processing.

Key words: Mechanochemistry, Material synthesis, Separation, Waste processing, Energy recovery

1. Introduction

When grinding is subjected to a material, the material is normally reduced in size, depending on its condition. In addition to that, the powder produced by this operation becomes active chemically. This chemical activation is called mechanical activation, leading to solid state reaction with another material without heating at certain condition. One of the conditions in the compression of the reaction is to overcome activation energy of the reaction system, and another one is that the Gibbs free energy change is minus. The former condition can be accelerated by heating, however, only grinding could be achieved the reaction in some cases. The advantage of the non-thermal solid state reaction is as follows: For example, it would avoid thermal decomposition of a material even if it has thermal property weaker than another in heating. Another advantage is to choose the arbitrary mixing ratio between two or more reaction systems. This means that it would be possible to enable to choose the molar ratio of the reactants selectable. The most peculiar advantage is to be simple in process for synthesizing a reaction product from the starting materials, due to simple grinding the materials under ambient condition.

We have synthesized many materials by grinding the starting ones in dry and wet conditions at different environments. In this paper, we would like to introduce a few examples of solid state reactions. Then, beneficiation of the mechanical activation induced by grinding is introduced for separating and generating useful substances from the starting materials: One is to separate and extract useful substances from the starting material by grinding followed by leaching the ground product, and another is to generate valuable gaseous components from the staring sample by grinding followed by heating at certain condition.
2. Solid-state reaction by grinding

There are many cases exemplified by ambient grinding condition. Direct synthesis by grinding is to proceed the reaction in boundary layer between two materials with elimination of the product in the boundary. The product may be aggregated one composed of fine particles, due to mechanical activation caused by the grinding. The primary particle size is about a few ten nano-meters.

2.1 Direct synthesis

One can take a result on grinding a mixture of CaO and TiO$_2$ by a planetary mill (Fritsch P-7, Germany), and Fig. 1 shows HR-TEM of the mixture milled for 5 hours$^{2–3}$. It is seen that the lattice distance of the product shown in the HR-TEM photo is 0.27 nm which is exactly the same as that of CaTiO$_3$. Fig. 2 shows XRD pattern of the mixture milled for different periods of time. In the figure, (A) is the mixture of CaO-TiO$_2$ (anatase), (B) the mixture of CaO-TiO$_2$ (rutile). The reactions in the both systems can be shown as below$^3$:

\[
\text{CaO + TiO}_2\ \text{(anatase)} = \text{CaTiO}_3, \\
\Delta G = -88.5 \text{ kcal/mol} \quad (1)
\]

\[
\text{CaO + TiO}_2\ \text{(rutile)} = \text{CaTiO}_3, \\
\Delta G = -82.3 \text{ kcal/mol} \quad (2)
\]

As can be seen from Fig. 2, the reaction system of (A) is easier than that of (B). This is materials function. It is necessary to increase the milling periods of time to achieve the reaction. Another example is a mixture of La$_2$O$_3$ and $B_2$O$_3$ ($B =$ Al, Fe, Cr, Mn, In and Ga) to form perovskite type compounds. The reaction is given by the following equations:

\[
\text{La}_2\text{O}_3 + \text{B}_2\text{O}_3 = \text{LaBO}_3, \\
(B = \text{Al, Fe, Cr, Mn, In, Ga}) \quad (3)
\]

In these reaction systems, completion of the reaction depends on the structure of $B_2$O$_3$. When $B_2$O$_3$ is corundum like Al$_2$O$_3$, the reaction does not proceed at all, but when $B_2$O$_3$ is non-corundum oxide, the reaction is achieved smoothly$^4–8$. Thus the reaction can be made by not only the necessary and enough conditions but also the type of structure of the materials to be synthesized. The reaction map in different reaction systems is shown in Fig. 3$^9$. It would be possible to estimate the completion of the reaction by the radius of the starting materials in the reaction systems. The product is aggregated powder, and it is possible to synthesize mono-dispersed fine particles of the product when the starting materials for grinding are salts and alcaline like NaOH. The process for producing nano-particles of LaCoO$_3$ without formation of

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**Fig. 1** HR-TEM photo and SED pattern of the mixture of CaO-TiO$_2$ milled for 5 h by a planetary mill

**Fig. 2** XRD patterns of the mixture of two compounds (a) CaO-anatase, (b) CaO-rutile

**Fig. 3** Relation between $k (=r_A/r_B)$ and $t =[(r_A + r_B)/2r_O]_0$ in the mechanochemical reaction systems
aggregation is shown by Fig. 4, and the reaction equation can be given by Eq.(4).

\[
\text{LaCl}_3 + \text{CoCl}_2 + 5\text{NaOH} = \text{La(OH)}_3 + \text{Co(OH)}_2 + 5\text{NaCl} \quad (4)
\]

When the product after grinding is heated at about 600°C, then the mixture of La(OH)₃ and Co(OH)₂ is reacted each other by eliminating H₂O, so that the sample powder after heating is composed of LaCoO₃ and NaCl. When the product is washed with water, the solid is a monodispersed one (20–30 nm in particle diameter) without aggregation, and NaCl is washed away by filtration.

Thus, one can image different reactions to form functional compounds such as TiO₂ doping with a small quantity of a material.

2.2 Grinding and leaching to separate useful compound from a starting material

A powder produced by dry grinding is in the activated state, due to mechanical activation caused by this operation. This activation would stimulate the following chemical and/or physical operation. In this section, we would like to introduce stimulation of chemical operation such as dissolution or leaching with water or acid solution of the ground product.

1) Leaching Mg and Si from talc ground

Talc is a mineral of magnesium silicate hydrate having chemical species Mg₃Si₄O₁₀(OH)₂. It is known that this mineral is changed its crystal structure into amorphous state when it is ground in air by a mill. Fig. 5 shows typical XRD patterns of the talc sample milled by a planetary mill (Fritsch, P-7, Germany). Its mineralogical structure is shown in Fig. 5. Thus, the structure is changed into amorphous state, implying that the milled powder is in activated one. This suggests that Mg can be dissolved in acid solution, while Si is remained in the structure when the ground product is dispersed in H₂SO₄ solution at 0.5 N, 298 and 333 K, and as a matter of fact, this suggestion has been materialized by Fig. 6.

Similar phenomena can be seen in the extraction of rare earths from the fluorescent powder of 3-wave length type and others.

2) Dechlorination of PVC with dechlorinating reagent like CaO

Polymer compounds like PVC and PE are normally difficult to reduce the particle size by only its grinding in ambient condition. However, when it is ground with inorganic compound such as CaO and NaOH, its particle size is reduced. In addition to this physical change, the chemical state in the boundary between the two materials is interacted chemically. For example, a mixture of PVC and CaO system is subjected to grinding in air for certain periods of time, the ground product is changed its chemical state. Fig. 7 shows dechlorination of PVC as a function of grinding periods of time when it is milled with CaO at two mixing ra-
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3. Concluding remarks

Grinding a material induces not only its size reduction but mechanical activation of fine particles. This operation enhances mixing degree of multi-materials when they are ground simultaneously in a mill. In this paper, grinding a material causes its structure change and/or solid state reaction to form another material like complex oxide. These products are normally activated powder, so that they

\[
\begin{align*}
\text{In}_2\text{O}_3 + 2\text{Li}_3\text{N} &= 2\text{In} + 3\text{Li}_2\text{O} + \text{N}_2 \tag{8}
\end{align*}
\]

The purity of In and its recovery are shown in Table 1.

### 2.3 Grinding and heating to generate hydrogen from biomass

Based on the comprehension of the advantages of the reported processes, we report a solid-state operation by milling cellulose (main component of biomass) with hydroxides of calcium and nickel. Hydrogen can be simply produced by heating the milled sample at temperature between 400~500°C with CO far less than 1%. This implies that a quite high transformation rate has been achieved even though the condition of non-steam reforming. Formation of the tar occurring with the gasification has been successfully avoided. Triggered by mechanical force\textsuperscript{13,14}, the simultaneous carbonate formation and hydrogen emission as well as in situ formation of Ni catalyst are understood as the new findings which contribute the presently efficient hydrogen production. Fig. 8 shows MS patterns of the gasses from cellulose sample heated at different temperatures after milling for 2 h. Table 2 shows gases emitted from cellulose by the process. The gas composition depends on the heating temperature, but when it is kept at 450~525°C, the concentration of H\textsubscript{2} is 93.5\%, while other concentrations are 6.4\% for CH\textsubscript{4} and below 0.1\% for CO and CO\textsubscript{2}. The yield of H\textsubscript{2} would be about 95\%, implying that most of H\textsubscript{2} in the cellulose sample is emitted as the gas. Besides cellulose, this process can be also applicable to other samples, as shown in Fig. 9\textsuperscript{23}.

### Table 1 Purity of In recovered and its recovery

| Grinding time (min) | In purity (%) | Li impurity (%) | Total (%) | In recovery (%) |
|---------------------|--------------|----------------|-----------|----------------|
| 30                  | 95.73        | 0.41           | 96.14     | 98.12          |
| 60                  | 96.76        | 0.37           | 97.13     | 97.25          |
| 120                 | 94.21        | 0.39           | 94.61     | 97.11          |
| 180                 | 94.25        | 0.29           | 94.54     | 97.39          |

Evaluation of purity and recovery for in-metal as a function of grinding time from data obtained by ICP analysis.

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are dispersed in liquid phase like water and/or acid or alkaline solution, so soluble compounds are extracted without even heating. Besides the few examples introduced in this paper, there have been many results. From these investigations, one can imagine that the grinding plays a big role to bring out many possible applications for material synthesis, material and waste processing.

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