JOURNAL OF MATERIALS SCIENCE **39** (2004) 5051 – 5055

Mechanochemical approach for preparing nanostructural materials

FUMIO SAITO*, QIWU ZHANG, JUNYA KANO
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
E-mail: saito@tagen.tohoku.ac.jp

Several mechanochemical methods for synthesizing nanostructural materials have been introduced in this paper. The methods are three different routes; one is a direct synthesis method, the second is a combination method, which composes of grinding, heating and washing, and the third is a doping one. Dry grinding a mixture facilitates the solid-state reaction (MC reaction), to form a product of fine particles with nanostructure of grains and their boundaries in lattice configuration. The micro-structure of material depends mainly on grinding energy and the composition of starting mixture. Under the grinding energy enough for mechanochemical synthesis, the synthesized material tends to be aggregated, so that the specific surface area (SSA) is not large. In order to increase the SSA, the combination method is recommended. The doping method is another concept, enabling us to cause a partial MC reaction in the fine particles. The chemical form and structure of the material depend mainly on a mixing ratio of the starting samples. The authors have attempted to form different functional materials such as catalysts from various starting samples by using a planetary mill, and introduced some of them in the present paper.

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1. Introduction

Much attention has been paid on nanostructural materials in these days, due to their unique properties. As particle size is reduced to nanometer range, the ratio of the atoms number facing on the surface to the whole atoms becomes high. This implies that influence of surface in nanoparticles is not ignored at all, and surface energy dominates powder behavior. The materials have normally been synthesized by high temperature and solution methods, such as vapor condensation techniques, combustion synthesis, thermo-chemical synthesis, sol-gel processing, and chemical precipitation. Recently, it has been reported that nanostructural materials can be synthesized by mechanochemical (MC) routes [1, 2]. This implies that mills, especially, fine grinders like a planetary mill are recognized as a tool for producing nanostructural materials, and the grinding is a key operation for such materials processing as well as the nanostructural materials preparation.

The main purpose of this paper is to introduce three methods for preparing nanostructural materials by means of the MC method. The first one is a direct method, the second is a combination method, and the third is a doping one.

2. Direct method for synthesizing nanostructural materials

2.1. Synthesis of complex compounds

Many reports have been published on the mechanochemical synthesis of complex oxides [3, 4]. The nonthermal merit and unnecessary control of the experimental atmosphere seems to be highly attractive for the synthesis of non-oxides, of which the inert gases or some specific gases are generally required. The first example is to show the MC synthesis of rare earth oxyfluoride, RE-OF (RE (rare earth) = La, Pr, Nd, Sm, Gd, Pr). The mixtures of oxide and fluoride with the same rare earth are mixed and they were ground in a planetary ball mill in air [5]. As a result, RE-OF can be synthesized from the mixtures, and XRD pattern of the LaOF synthesized is shown in Fig. 1 with TEM-SAED pattern shown in Fig. 2. Furthermore, LaOF can be also synthesized from a mixtures of La_2O_3 and polymers such as PVDF ($[\text{-}CH_2CF_2\text{-}]_n$) and PTFE ($[\text{-}CF_2CF_2\text{-}]_n$) [6, 7]. The advantage of this route is to obtain LaOF nanoparticles by burning out the hydrocarbon and other intermediates formed in the ground product. Other rare earth oxyhalides can be synthesized mechanochemically by the similar way. In addition, solid solutions like $LaOCl_{1-x}Br_x$ ($x = 0$–1) are able to be synthesized

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*Author to whom all correspondence should be addressed.

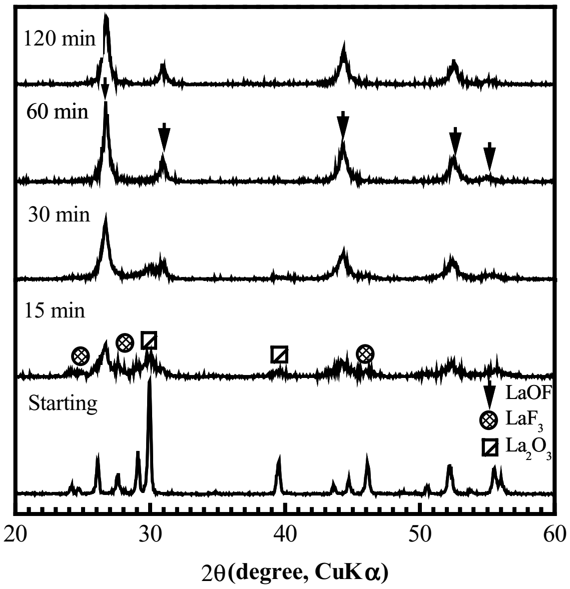

Figure 1 XRD patterns of the mixture of La_2O_3 and LaF_3 ground for different periods of time.

from a mixture of $LaCl_3$ and $LaBr_3$ [8]. Similarly, perovskite structural fluorides materials, given by $AM^{II}F_3$ ($A = Na, K, NH_4$, $M^{II} = Mg, Zn$) [9] can be synthesized from a mixture of alkali metal fluoride (AF) and transition metal fluoride ($M^{II}F_2$) by the direct method.

2.2. Transformation of oxide into non-oxide compounds

It is known that oxides are normally more stable than the corresponding sulphides. It is easily to oxidize the sulphides into oxides. On the contrary, it is difficult to transform oxides into sulphides. In the case of nonferrous metal ($M = Pb, Zn, Cd$) oxides, the sulphidization is useful for the recovery of these metals from industrial wastes because the existing metallurgical technologies are based on the sulphide processing. Therefore, the authors have developed a mechanochemical method for sulphidizing the oxides. The method is based on co-grinding of corresponding oxide with sulfur and iron and stimulation of solid-state reaction to form nonferrous metal sulfides and iron oxide [10]. The reaction shown below proceeds with an increase of grinding time, as shown in Fig. 3 for zinc oxide. All other oxides have been sulphidized to the corresponding sulphides. $CuFeS_2$ has been the final product in the case of copper oxide.

$$4MO + 4S + 3Fe = 4MS + Fe_3O_4; \quad (M = Zn, Pb, Cd) \qquad (1)$$

The necessary conditions to sulphidize the oxides have been clarified based on the thermodynamic discussion. Both reactions of iron sulphides formation and sulphidization of oxides were defined and the changes in ΔG_{298} were compared and summarized in Table I. Comparison of ΔG_{298} changes between the successful sulphidization reaction and the iron sulphides

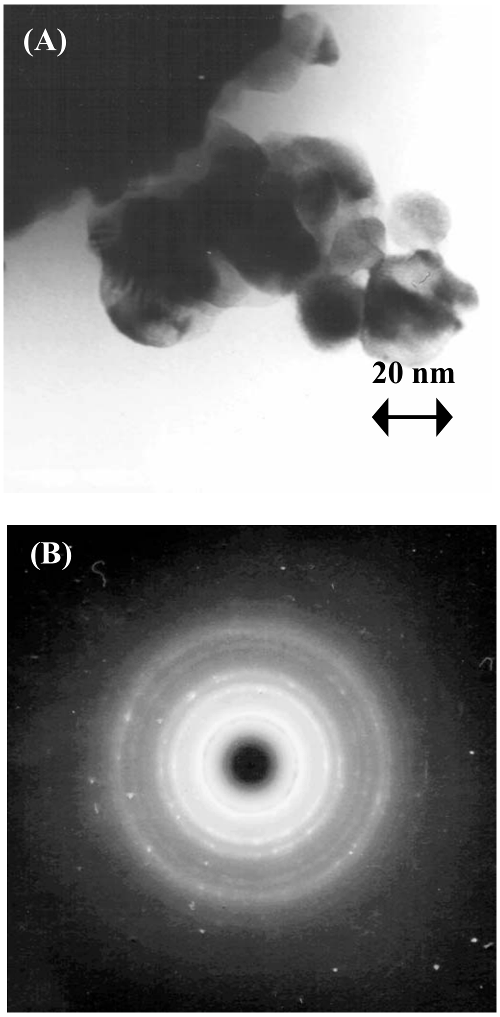

Figure 2 TEM-SAED profiles of the 60 min ground mixture: (A) bright field image and (B) selected area electronic diffraction.

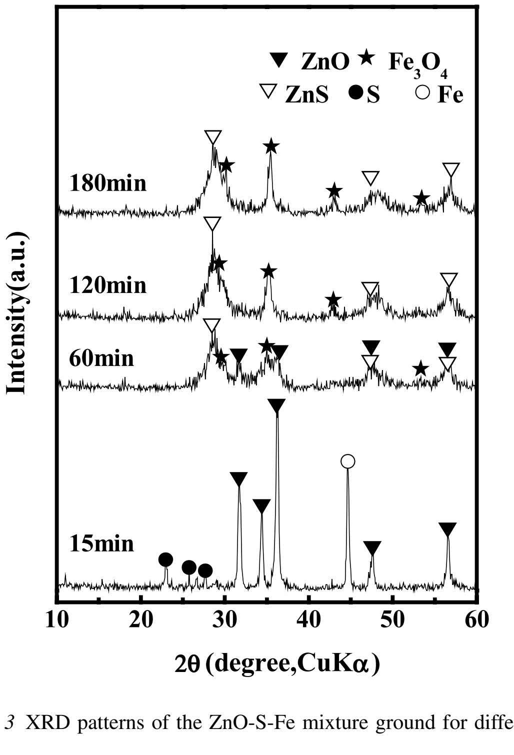

Figure 3 XRD patterns of the ZnO-S-Fe mixture ground for different times.

TABLE I Comparison of the values of ΔG_{298} for corresponding reactions

Starting material	Reaction	ΔG_{298} (kJ/mol)
CdO	$4CdO + 4S + 3Fe = Fe_3O_4 + 4CdS$	−673
	$4CdO + 4S + 3Fe = 4CdO + FeS + FeS_2$	−364
PbO	$4PbO + 4S + 3Fe = Fe_3O_4 + 4PbS$	−649
	$4PbO + 4S + 3Fe = 4PbO + FeS + FeS_2$	−364
ZnO	$4ZnO + 4S + 3Fe = Fe_3O_4 + 4ZnS$	−535
	$4ZnO + 4S + 3Fe = 4ZnO + FeS + FeS_2$	−364

formation indicates not only the negative changes in ΔG_{298} values but also higher thermodynamical probability for metal sulphidization in comparison with the iron sulphide formation. It can be summarized as a necessary condition to sulphidize a specific oxide that there exists a larger negative change in ΔG_{298} of the designed sulphidizing reaction than that of the iron sulphides formation. This thermodynamic condition is just a necessary but sufficient one. Whether or not an oxide can be sulphidized by this method depends on the crystal structure. Several other reports have been published on the dependence of the MC reaction on the crystal structure of the starting materials. Based on the sulphidizing process, it is expected that the current mineral processing technologies such as flotation and magnetic separation can be used to recover the metals from various kinds of wastes or to purify the contaminated wastes when the heavy metals inside, such as lead cadmium etc., are sulphidized and removed. Similar to Fe powder, the use of Al powder also brings about the transformation of the oxides into corresponding sulphides, being accompanied by the formation of Al_2O_3. ΔG_{298} of sulphidizing reaction is −1223.6 kJ/mol (−407.9 kJ per mol of ZnO). Although it is economically impossible to use pure aluminum as additive to treat waste, this method offers a new approach to treat aluminum dross waste, which remains as an environmental problem for aluminum industry and needs proper treatment.

3. Combination method

An example is to show the formation of $LaCoO_3$ from a mixture of $LaCl_3$, $CoCl_2$ and NaOH. Of course, $LaCoO_3$ can be synthesized by the direct method, but the specific surface area (SSA) of the final product is only about 3 m^2/g. The authors have attempted to increase the SSA value to more than 10 m^2/g by the combination method, which is composed of grinding, heating and washing operations. XRD patterns of the each sample are shown in Fig. 4. It is noticed from the XRD pattern of (a) that $La(OH)_3$ and NaCl are formed in the ground product. The reason why the peaks of $Co(OH)_2$ do not appear may be due to its amorphous character. The MC reaction has been facilitated by the grinding the starting samples, as given by Equation 2

$$LaCl_3 + CoCl_2 + 5NaOH = La(OH)_3 + Co(OH)_2 + 5NaCl \quad (2)$$

It is deduced that an activated precursor-like mixture with well-dispersed NaCl particles is formed in the ground product. According to the XRD pattern of (b), $LaCoO_3$ and NaCl are formed in the heated sample, and the reaction during the heating can be given by Equation 3

$$La(OH)_3 + Co(OH)_2 + 5NaCl + 0.25O_2 = LaCoO_3 + 2.5H_2O + 5NaCl \quad (3)$$

Usually, $LaCoO_3$ has been synthesized by heating at around 1200 K when the constituent oxides like La_2O_3 and Co_2O_3 are used as starting materials. In comparison with this, the temperature of 873 K in the present work is extremely lower than as usual. This may be due to the MC effect induced by the grinding. As for the pattern of (c), it is found that only peaks of $LaCoO_3$ are present, suggesting that NaCl has been removed away from the product by the washing and filtration operation.

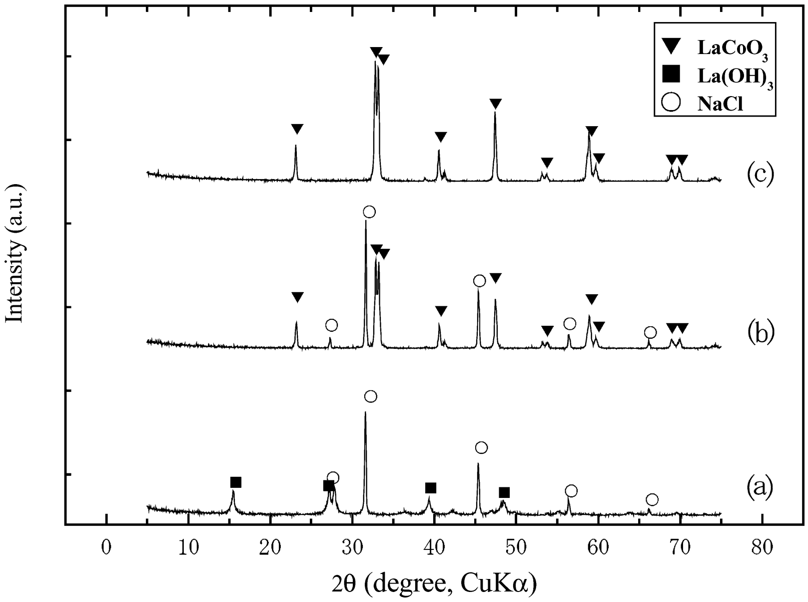

Figure 4 XRD patterns of La-Co-O samples from the three steps: (a) the mixture ground for 3 h; (b) the sample heated at 873 K for 1 h after 3 h grinding operation; and (c) the sample washed after the grinding (3 h) and heating (873 K for 1 h) operations.

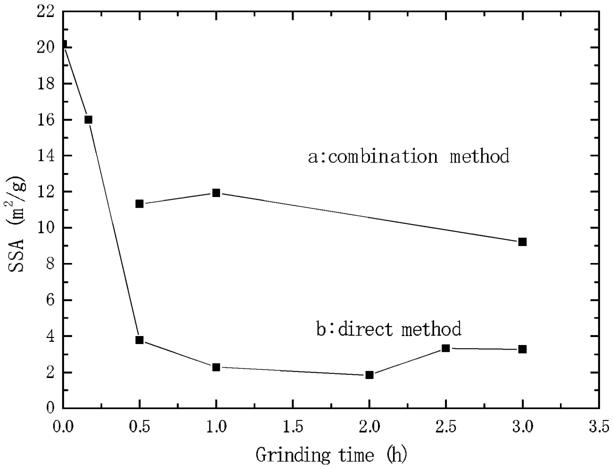

Figure 5 Comparison of the specific surface area (SSA) of the $LaCoO_3$ samples prepared by two methods.

Fig. 5 shows the SSA of the final products together with those obtained by the direct method. According to the result, $LaCoO_3$ has been formed in the ground product by the both methods, and 3 h grinding is enough to form the target material ($LaCoO_3$) in the ground products. The SSA of the product obtained by the combination method is about 10 m^2/g. Fig. 6 shows SEM micrographs of the two kinds of product obtained by the combination and the direct methods, respectively. It is seen that the morphology in the product (a) is relatively finer than that in the product (b). Therefore, it is recommended that the combination method is superior to the direct one in terms of the synthesis of fine $LaCoO_3$ powder.

4. Doping oxide with nonmetal element

Compared with the intensive investigations on the cation doping, recent reports concern about the doping of TiO_2 with nonmetal elements such as nitrogen, fluorine, sulphur, and carbon [11–13]. Activity in the visible-light region of the doped TiO_2 samples has been found to correlate with the shift of absorption edge of the light to a lower energy region. It is well known that TiO_2 is generally a stable compound, and not easily doped by a nonmetal element. It is particularly difficult for TiO_2 to dope atom of big size such as sulfur. In order to dope nonmetal elements into TiO_2, one can heat TiO_2 at high temperature under gaseous environment such as NH_3, H_2S. However, the calcination of TiO_2 under H_2S gas flow does not give always satisfactory results. Heating of TiS_2 in air has been proposed to prepare S-doped TiO_2, but the preparation of TiS_2 itself is not easy, and it brings about enormous emission of SO_2 gas.

Our research has revealed that mechanochemical treatment of TiO_2 with sulphur, followed by heating at 673K allows to dope easily non-metal elements to the oxide (TiO_2). Although not shown here, the phase transformation of anatase to rutile has been observed by the mechanical operation according to the XRD analysis. Fig. 7 shows XPS spectra of the S2p state of the mixtures ground for 20 and 120 min. The S2p state has a broad peak because of the overlap of the split sublevels, the 2p3/2 and 2p1/2 states, with separation of 1.2 eV by spin-orbit coupling [14, 15]. As has been observed in the two spectra, two peaks appear at around 169 and 162 eV, respectively. But the peak position at low energy for the sample ground for 20 min is slightly different from that for 120 min. The former peak is located around 165–163 eV, whilst the other is positioned around 163–161 eV. On the other hand, there is not significant difference in the peak position at high energy region between the spectra of both samples. According to the several reports [14, 15], the peak positioned around 169 eV is due to the absorbed SO_2 molecules on the TiO_2 surface and the peak around 162 eV results from the bonding between S and Ti atoms. It is known that sulfur exhibits usually the peak position around 164 eV. Therefore, the short time grinding (20 min) is not effective for doping S, because S—S bonding

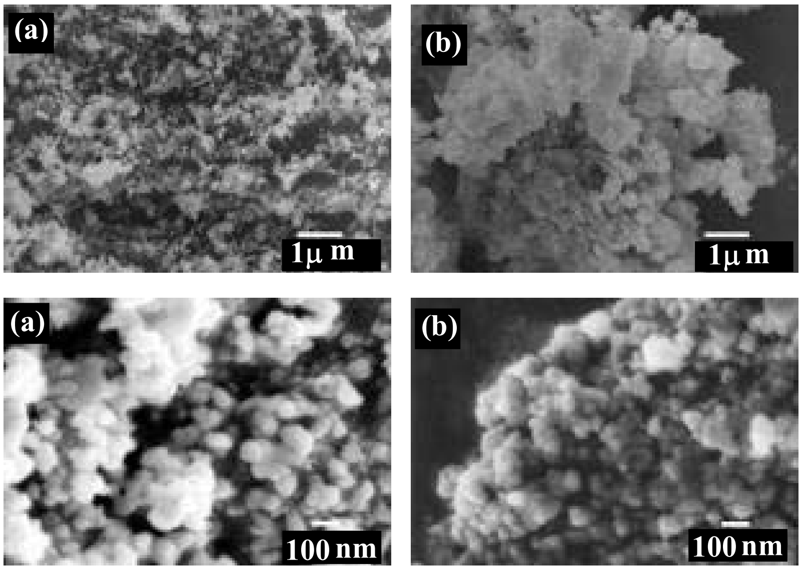

Figure 6 SEM photographs of the two kinds of product: (a) product after grinding for 3 h, heating at 873 K for 1 h and subsequent washing; and (b) product by the direct mechanochemical reaction.

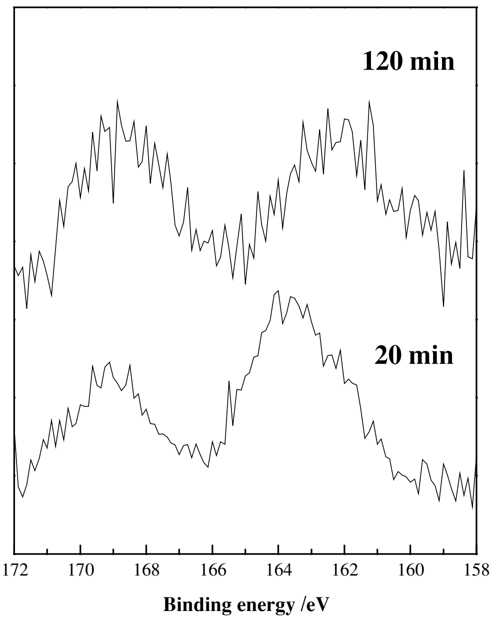

Figure 7 XPS spectra of the samples ground for 20 and 120 min.

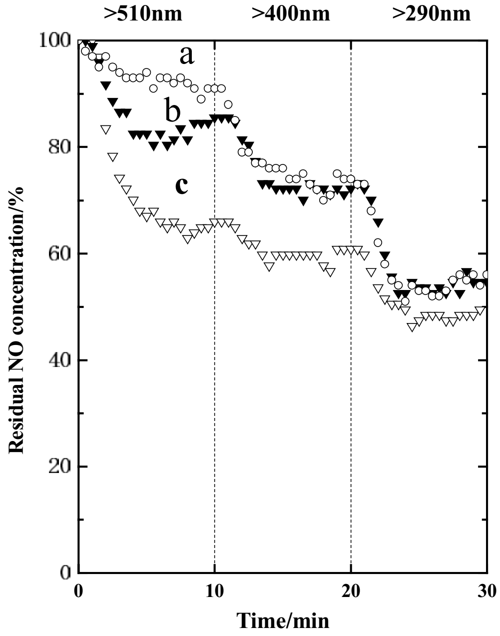

Figure 8 The relationship between light wavelength and the photocatalytic ability for the oxidation of NO of the prepared samples: (a) 120 min ground TiO_2; (b) co-grinding with sulfur for 20 min; and (c) co-grinding with sulfur for 120 min.

remains as the main composition. Prolonged grinding is crucial operation to ensure the formation of S—Ti bonding.

Fig. 8 shows the relationship between the wavelength of light source and the remaining percentage of NO gas for the S-doped TiO_2 samples (b) and (c), and the sample (a) as a reference. It is clearly observed that the reference sample (a) exhibits low photocatalytic activity by the irradiation of light with wavelength over 510 nm. On the contrary, about 20% NO has been removed in the range of the wavelength over 510 nm for sample (b), while nearly 40% NO is decomposed for sample (c). This means that sample (c) has a high photo-reactivity under visible-light irradiation. The photocatalytic activity for the prepared samples is found to be almost the same as that of the reference sample under ultraviolet light. Similarly, the N-doped TiO_2 samples can be synthesized from a mixture of TiO_2 and nitrogen-containing compounds (for example, urea, hexamethylenetetramine) by the present doping method [16], and it has exhibited excellent photocatalytic activity for decomposition of NO under visible light wavelength region, as similar to the N-doped TiO_2 ones.

5. Conclusion

In the present paper, three mechanochemical methods for synthesizing nanostructural functional materials have been introduced. The first direct method is of course well known, so that many investigations have been made so far. As for the second one, the combination method is based on an unique concept to prepare the nanostructural materials, so that it is expected to apply to other reaction systems more and more. The last method is a doping, which is controlled by the mixing ratio of the starting sample as well as the grinding condition, and it has also a potential to synthesize many different material systems. It has not shown in this paper, but it is very important that wet milling is another important operation to form nanostructural materials. Anyhow, mechanochemistry has a lot of potential to synthesize materials, which exhibit unique and excellent properties, and it is a great expectation to come.

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Received 11 September 2003
and accepted 27 February 2004