

Spectroscopic studies on the formation kinetics of SnO₂ nanoparticles synthesized in a planetary ball mill

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Abstract

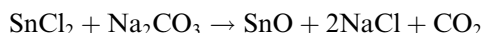
SnO₂ nanoparticles with an average diameter of 9 nm were synthesized by the mechanochemical reaction between SnCl₂ and Na₂CO₃ in a planetary ball mill. The pressure and the temperature were continuously monitored in the milling drum and the reaction products were characterized by TEM, SEM, FT-Raman, mid-IR and far-IR spectroscopy. The pressure in the drum was found to be a highly nonlinear function of the milling time. This finding could be adequately explained on the basis of the spectroscopic evidence collected. We suggest that the speed of the mechanochemical reaction is given by a fast-slow-fast(-slow) series which is caused by the variation of the wetness of the reaction mixture during milling. The measured pressure nonlinearity is thus a direct consequence of the kinetics of the mechanochemical reaction.

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1. Introduction

SnO₂ nanoparticles are intensely studied nowadays because of their advantageous sensing properties. Sensors aimed at detecting e.g. ethanol [1,2], LPG, CNG [3] and CO [4] have been realized by several groups. SnO₂ nanoparticles can be prepared by a broad variety of synthesis techniques including hydrothermal treatment [5], thermal decomposition [6] and the sol–gel process [7]. It is also possible to prepare the nanoparticles by mechanochemical synthesis [8] when performing the following reaction [9] in a high impact planetary ball mill:



and heat treating the product mixture in oxygen to get SnO₂. This reaction offers good control over the morphology and the size distribution of the resulting nanoparticles and therefore, it is currently investigated in our group.

In particular, we are interested in uncovering the details of the kinetics of tin-oxide formation by continuously monitoring the temperature and pressure in the milling jar during reaction, and analyzing the structure of the products by mid-IR, far-IR and Raman spectroscopy as well as electron microscopy. In this contribution, we report on the effect of milling time on the vibrational spectroscopic properties of the products. These results help us interpret the pressure vs. time curves recorded during the mechanochemical reaction.

2. Experimental

The mechanochemical tin-oxide synthesis was done in a 250 cm³ stainless steel milling drum containing 50 stainless steel balls of 10 mm diameter. The drum was filled with a mixture of 8.37 g SnCl₂·2H₂O, 3.94 g Na₂CO₃ plus 13.01 g NaCl matrix and rotated at 400 rpm in a FRIT-SCH Pulverisette 6 planetary ball mill. The function of the NaCl is to prevent the aggregation of the reactant and product particles [10]. Pressure and temperature within

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the drum were continuously monitored by a GTM II head and sent to a personal computer by radio transmission. The end product of the mechanochemical reaction was calcined in O₂ flow for 2 h at 600 °C and washed in distilled water on a 0.45 μm PTFE membrane filter. Experiments were repeated three times in order to exclude measurement artifacts from the analysis.

Transmission Electron Microscopic (TEM) observations were performed on a Philips CM10 instrument using copper mounted holey carbon grids. Scanning Electron Microscopy (SEM) was done on a Hitachi S-4700 field emission scanning electron microscope on uncoated samples. FT-Raman spectra were averaged from 256 scans performed at 4 cm⁻¹ resolution on a Bio-Rad FT-Raman instrument operating with 1064 nm excitation wavelength at room temperature in air. FT-IR (mid-IR range) spectra were taken with a Mattson-Genesis 1 instrument (256 scans, 4 cm⁻¹ resolution) using the KBr pellet technique. Far FT-IR spectra were measured on a Bio-Rad FTS-65v instrument (256 scans, 4 cm⁻¹ resolution) in polyethylene pellets. Vibrational spectra were baseline subtracted and normalized to their largest peaks to facilitate comparison.

3. Results

It is customary in mechanochemistry to let a synthesis run for a predetermined amount of time and sample the product mixture at regular intervals. This approach is based on the assumption that the studied reaction is progressing linearly in time. In the case of mechanochemical SnO synthesis, however, the total pressure in the milling drum is a highly nonlinear function of time as shown in Fig. 1. and therefore, it is likely that the synthesis reaction is subject to some interesting kinetics itself. In the first 5 min the pressure is increasing steeply while the temperature remains constant. This initial period is followed by a longer section when both pressure and temperature rise linearly. After ≈50 min the pressure in the drum rises in an abrupt step and the temperature reaches its maximum value. The reaction is concluded by another, shorter linear

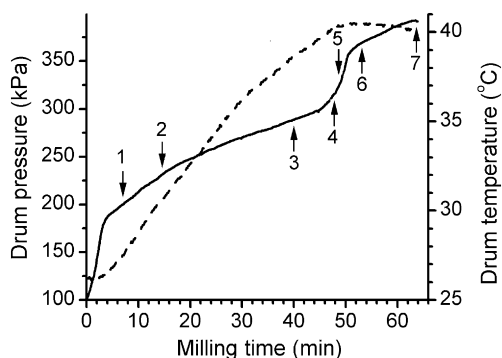


Fig. 1. Pressure (solid line) and temperature (dashed line) of the atmosphere in the milling drum during the mechanochemical synthesis of SnO₂ nanoparticles. Samples discussed in this report were taken at points denoted by arrows on the pressure curve (see Table 1 for details).

pressure increase section. Neither the pressure nor the temperature changes significantly if the mill is allowed to run longer than 65 min (not shown).

The reaction mixture contained stoichiometric amounts of SnCl₂ and Na₂CO₃. In a control experiment, the mill was run using parameters identical with those of the reaction but without tin(II)-chloride. The purpose of this experiment was to (i) prove that the self-decomposition of Na₂CO₃ is insignificant under the reaction conditions, and (ii) to obtain the $p_{\text{air}}(T)$ function which describes the pressure increase due to the warming up of the air atmosphere in the drum. In the mechanochemical SnO synthesis experiments, the partial pressure of the CO₂ was calculated as $p_{\text{CO}_2}(T) = p_{\text{total}}(T) - p_{\text{air}}(T) - p_{\text{H}_2\text{O}}(T)$, where $p_{\text{total}}(T)$ is the total pressure measured by the GTM II head, $p_{\text{air}}(T)$ is the partial pressure of the air enclosed in the drum and $p_{\text{H}_2\text{O}}(T)$ is the vapor pressure of water (originating from SnCl₂·2H₂O) at the measured temperature T . By introducing this latter quantity we assume that there exists a water vapor–liquid equilibrium within the drum. Considering the relatively large amount of available H₂O and the low temperature (barely exceeding 40 °C) of the drum atmosphere, this hypothesis seems reasonable.

Since CO₂ is only generated by the reaction of SnCl₂ and Na₂CO₃, the amount of CO₂ formed is proportional to the amount of SnCl₂ reacted. Therefore, it is possible to calculate SnCl₂ conversion (defined as the amount of reacted SnCl₂ over the original amount of SnCl₂) from the CO₂ partial pressure. We decided to sample the reaction products at certain special points of the conversion vs. time curve as indicated by the arrows in Fig. 1 and the numerical data in Table 1. It was believed that analyzing the reaction mixture in these particular points may help us understand the unexpected nonlinear behavior of the mechanochemical reaction.

The end product of the reaction after calcination was nanoparticulate SnO₂ with a mean diameter of 9 nm as determined from the analysis of three independent TEM images (see Fig. 2A for a characteristic example) by measuring at least 50 particles on each image. The individual SnO₂ nanoparticles aggregated into μm-sized assemblies as exemplified by the high resolution SEM image in Fig. 2B. Aggregation was most likely the result of the washing of the calcined reaction products on membrane filters to eliminate NaCl and any unreacted material.

Table 1
An overview of the samples studied in this report

Sample	Milling time (min)	SnCl ₂ conversion (%)
1	8	37
2	15	40
3	40	63
4	50	80
5	52	87
6	55	98
7	65	99

SnCl₂ conversion is calculated from the pressure measured in the milling drum.

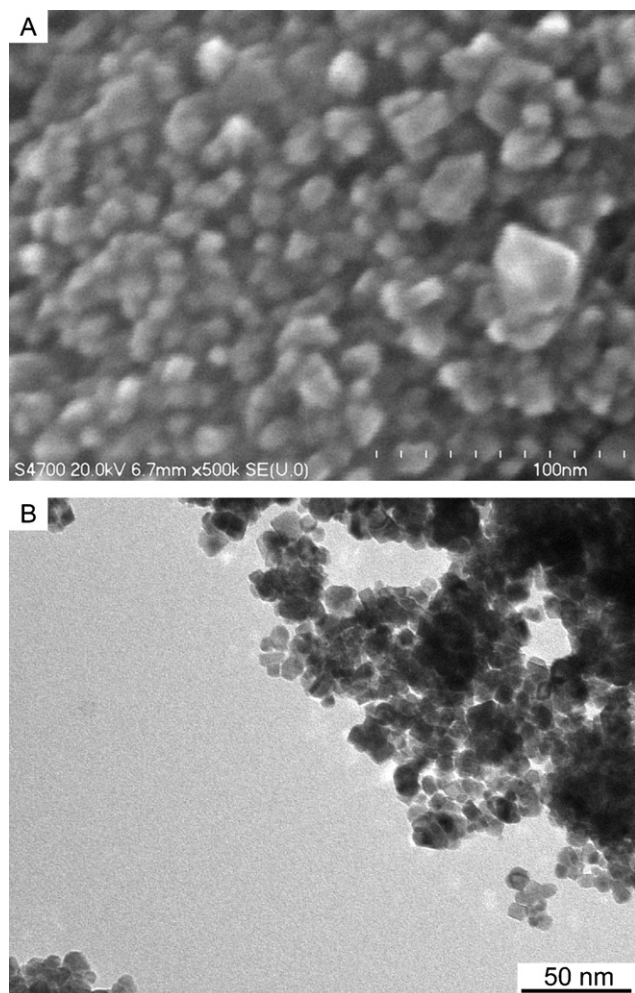


Fig. 2. Scanning (A) and transmission (B) electron micrographs of SnO₂ nanoparticles (sample 7C) obtained after 65 min mechanochemical reaction and 2 h calcination in O₂ flow at 600 °C.

The FT-Raman spectra of three selected calcined samples corresponding to 37%, 87% and 99% SnCl₂ conversion are presented in Fig. 3. The spectra are rather similar and feature common peaks at 473, 560 and 630 cm⁻¹. The main differences are the weakness of the 254 and 304 cm⁻¹ peaks

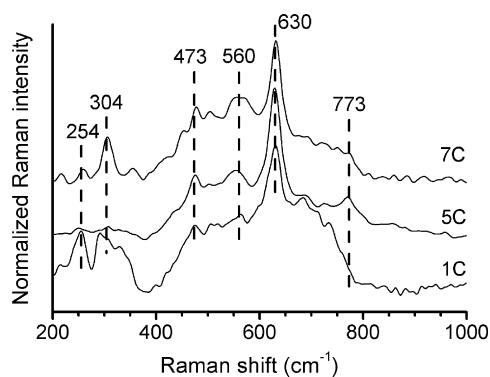


Fig. 3. FT-Raman spectra of three selected SnO₂ nanoparticle samples (see Table 1 for labeling).

in the 5C spectrum and the absence of the shoulder at 773 cm⁻¹ from the 1C spectrum. The low wavenumber peaks (304 and 254 cm⁻¹) were suggested earlier to be related to the aggregation of SnO₂ nanoparticles [11]. Since in our case aggregation takes place only during the filtration of the calcined samples, there is no direct correlation between the synthesis time and the intensity of these spectral features.

It is more rewarding to study the mid-IR spectra of the whole uncalcined sample series presented in Fig. 4. Each spectrum contains a broad and intense ν_{O-H} signal group between 3000 and 3600 cm⁻¹ and several intermediate and high intensity peaks in the fingerprint region between 800 and 400 cm⁻¹. Spectra 1A–3A have peaks at 1445, 877, 702, 472 and 426 cm⁻¹. On the other hand, in spectra 4A–7A the 1445 and 877 cm⁻¹ peaks are practically missing, while the 1624 and 607 cm⁻¹ peaks become very strong. The 702, 472 and 426 cm⁻¹ features are gradually reduced to shoulders with increasing milling time.

The IR spectra of the washed and calcined SnO₂ samples (Fig. 5) are dominated by three peaks at 660, 621 and 528 cm⁻¹ and have additional smaller features at 1626 and 3426 cm⁻¹. The most pronounced effect of increasing milling time on the spectra is the intensity increase of the 660 and 528 cm⁻¹ features relative to the 621 cm⁻¹ one. In the far-IR region (Fig. 5, inset), the spectra of samples 1C, 5C and 7C appears very similar with peaks at 250, 290, 341 and 470 cm⁻¹.

4. Discussion

The first question one must address is if the calcined end-products of the mechanochemical reaction obtained using different milling times can be considered the same material or not. Energy dispersive X-ray spectroscopy (EDS) performed within the SEM instrument (results not shown) indicated that the elemental composition of each sample was close to Sn:O = 1:2. The FT-Raman spectra

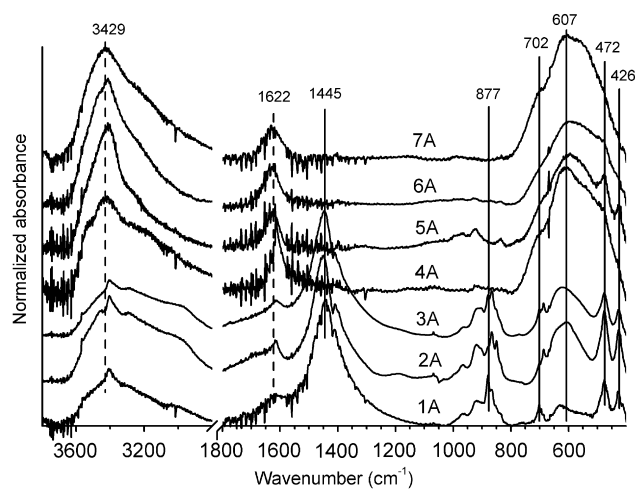


Fig. 4. FT-IR spectra of the uncalcined ("A" series) reaction products obtained using different milling times (see Table 1 for details).

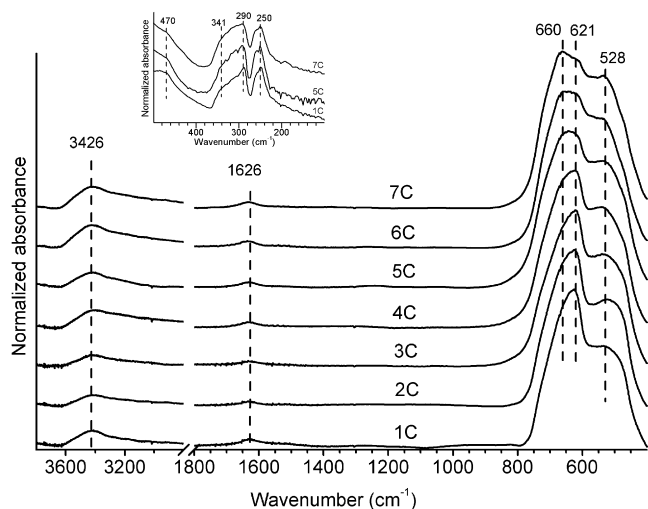


Fig. 5. FT-IR spectra of the calcined (“C” series) reaction products obtained using different milling times (see Table 1 for details). The inset shows the far-IR spectra of three selected samples.

(Fig. 3) of samples 1C, 5C and 7C are very similar. The peaks at 630, 773 and 473 cm^{-1} can be identified as the A_{1g} , B_{2g} and E_g Raman active modes of SnO_2 , respectively [12]. The mid-IR and far-IR spectra (Fig. 5) of the calcined samples are also similar. In this case, the 470 cm^{-1} peak is identified as the A_{2u} mode, the 250, 290, 621 cm^{-1} bands correspond to the transverse optical (TO) $E_u(1)$, $E_u(2)$ and $E_u(3)$ modes and the 341 cm^{-1} shoulder is assigned to the longitudinal optical (LO) $E_u(2)$ mode. The LO $E_u(1)$ and $E_u(3)$ modes are also noticeable as shoulders at 262 and 710 cm^{-1} , respectively [12]. The 1626 and 3426 cm^{-1} peaks belong to the bending and stretching modes of terminal OH groups on the SnO_2 surface. The peaks at 528 and 660 cm^{-1} can be assigned to surface modes of the nanoparticles [13]. These appear in the spectra specifically because of the very small particle size achievable by the mechanochemical synthesis. All this evidence makes us conclude that regardless of the milling time, the calcined end-product of the mechanochemical reaction is nanoparticulate SnO_2 .

We can now turn the second question, the nonlinearity of the pressure vs. time curve measured during the mechanochemical reaction. The infrared spectra of the as-synthesized materials are presented in Fig. 4. The 1445 cm^{-1} peak belongs to nonsymmetrical in-plane vibrations of the carbonate ion. This mode is originally of E' symmetry but is split into $A+B$ modes because of the crystal field [14]. The 879 cm^{-1} peak is also assigned to an internal carbonate mode: it belongs to a B_u mode derived from an A'_2 mode by crystal field splitting. The original A'_2 mode corresponds to polar movements perpendicular to the plane of the ion [14]. The third internal carbonate mode is observable at around 702 cm^{-1} . This vibration is assigned to the split components of a doubly degenerate E' mode corresponding to the in-plane carbonate vibrations [14]. Therefore, it is clear that in the regime of quasi linear pressure

increase (samples 1A–3A) the system contains unreacted Na_2CO_3 , which disappears at the beginning of the abrupt pressure increase step (spectrum 4A). Its disappearance coincides with the pronounced increase of the intensities of the 607 cm^{-1} peak assigned to tin oxide and of the 1622 and 3429 cm^{-1} O–H bending and stretching modes, respectively. Moreover, the rotational transitions of free H_2O are observable superimposed on these bands in the 4A–7A spectra. It should be noted that free H_2O rotations were also observable at the very beginning of the synthesis (1A) but not in the linear pressure increase regime (2A and 3A). Water is introduced into the drum with the SnCl_2 reagent and – to a much smaller extent – with the dampness of air and the other two reactants.

On the basis of these findings we suggest that the key to understanding the studied mechanochemical reaction is the role of water in the milling drum. A small amount of water is released from the reactants as soon as the mill is started, thus in the first few minutes the system is running in wet grinding mode which results in a fast reaction. It is common knowledge in mechanochemistry that wet grinding is more advantageous than dry grinding because of the more effective energy transfer from the balls to the reactants [15,16]. Consequently, the pressure doubles in the drum during the first 8 minutes of the reaction. Spectral features assigned to Na_2CO_3 are observable at this stage because the total conversion is still low. Later, the continuous energy transfer from the mill to the reactant mixture (and the released reaction enthalpy, to a much smaller extent) increases the temperature in the drum. When enough water is evaporated, the system switches to the less effective dry grinding mode resulting in a slower reaction rate. This is the region between 8 and 44 min when the pressure increases linearly with time. However, the running reaction continuously frees water up from the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ crystals. At some point (above 80% conversion in our case) there will be enough water in the system to switch back to wet grinding mode again. The reaction speeds up again and consumes most of the still available Na_2CO_3 very fast. This explains the steep pressure increase step between 46 and 50 min and the absence of the carbonate peaks from the mid-IR spectra of the 4A–7A samples. The reaction is concluded by another slower section, when the system is still in wet grinding mode but the conversion is so high that almost all reactants are consumed. Therefore, the rate determining step here is not the effectivity of the energy transfer from the mill to the compounds but rather, the probability of a successful meeting of the two reactants.

5. Conclusions

We have studied the formation kinetics of SnO_2 nanoparticles in a mechanochemical reaction in which CO_2 is released. SnO_2 nanoparticles were formed after calcination regardless of the milling time. The surprisingly non-linear behavior of the pressure vs. time curve could be explained on the basis of a detailed IR spectroscopic study. We suggest

that the system first runs in wet grinding mode, then switches to dry grinding and back to wet grinding again. Since mechanochemical reactions run faster in wet grinding mode because of the more efficient energy transfer, the reaction rate also changes in a fast-slow-fast(-slow) fashion which is mirrored in the CO₂ release rate and consequently, in the measured pressure vs. time curve.

Acknowledgements

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