MECHACHEMISTRY FOR CATALYSIS: PREPARATION OF PEROVSKITE STRUCTURAL MATERIALS AND MIXTURES OF METAL OXIDES

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Abstract

The main task of our research was the production and investigation of mechanochemically produced perovskite-structured materials and mixtures of metal oxides. Our goal is to develop a general synthetic method suitable for the large-scale production of many such materials. For this we have at our disposal a high-energy planetary ball mill, as well as an in-situ pressure and temperature measuring system that greatly facilitates the follow-up of the process. In addition we also used a model describing the synthesis conditions in a context suitable for determining the grinding energy developed and verified in part by us.

Introduction

About 85% of industrial processes are based on some kind of catalytic process, which is due to maximizing product yields, speeding up production processes and preventing waste generation. As a result, global catalyst sales have now exceeded $ 35 billion a year. Researchers are only able to satisfy the industry's unquenchable catalyst hunger with continuous improvement, so the basic goal is to produce such materials that can be produced cheaply and in large quantities.

Mechanochemistry is one of the processes in which kinetic work is translated into the transformation of various materials. This is mostly one of the structural synthesis methods that can be used to create particles in the nanometer range. A common feature of perovskites is the structure represented by the general formula $^{XII}A^{2+VI}B^{4+}X^{2-}_3$. Their versatility is due to the fact that many elements can be incorporated into the crystal lattice lattice, so that their properties can be changed. Their application is not only limited to cheaper solar cells, but can also be used as a sensor and even a catalyst. Similarly, metal oxides and their mixtures play a prominent role among catalysts.

Experimental

We pointed to the synthesis of metal-oxide and perovskite nanoparticles by the mechanochemical reaction in a planetary ball mill (Fritsch Pulverisette 6 planetary ball mill) is suited for fast and high-yield production. Besides the metal-salt precursor Na_2CO_3 and NaCl matrix was applied also. The latter bulks large in the separation of the nanoparticles and in the energy transmission. We state by numerous measurement method (XRD, FT-IR, Raman, TEM, SEM) that the products have uniform morphology and monodisperse size distribution (10 ±5 nm) and after preparation extractable by simple washing. We successfully applied this method to synthesise SnO_2, ZnO, TiO_2 metal-oxide and $BaTiO_3$, $ZnTiO_3$ or $NaNbO_3$ perovskite structured nanoparticles.

In the course of our work, our goal was to follow the mechanochemical processes in time with a pressure and temperature measuring head (GTM), which can be mounted specifically on the grinding drum. Thus, the knowledge of the reaction kinetics was expected to be expanded, and a significant shortening of the optimization process was expected with the help of the measuring unit (Fig.1). We tried to prove that the GTM head can trigger the

optimization of the synthesis of a product in one step, which is only possible in several steps with XRD or TG techniques.

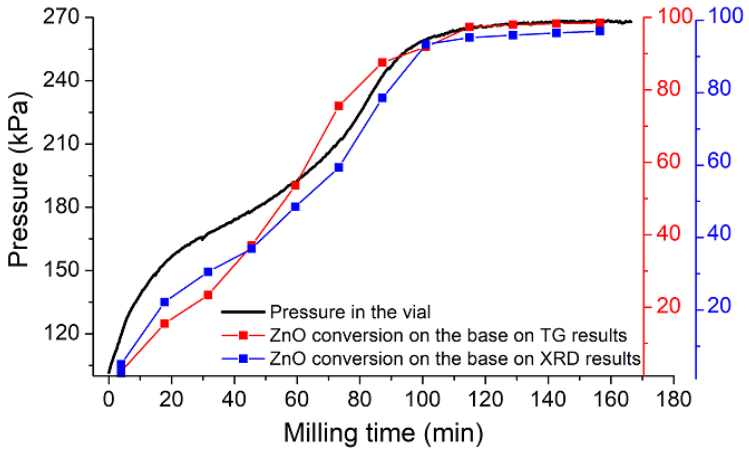

Fig.1: Pressure curve in the vial during the preparation of ZnO, and the conversion of ZnO based on the TG and XRD measurements.

We performed the production of different nanoscale perovskite structures in a planetary ball mill. Each of the produced materials was characterized in detail, their properties and the reproducibility of the mechanochemical process were investigated.

Results and discussion

In the initial phase, $ZnTiO_3$ was prepared in two steps. $ZnCl_2$ is mechanochemically converted to $ZnCO_3$ as an intermediate and then to ZnO by high energy ball milling. TiO_2 was prepared directly from $TiCl_4$ by mechanochemical means. With the precise control of the grinding energy, it was also possible to produce pure anatase and rutile phase TiO_2. We also produced titanate nanofibers and nanotubes from TiO_2 by the method developed in our department by hydrothermal means. This provided us all the starting materials. In the second step, the mechanochemical treatment of samples with different precursor compositions were performed. In all case the product was $ZnTiO_3$. The preparation was monitored by X-ray diffraction measurement (Fig.2).

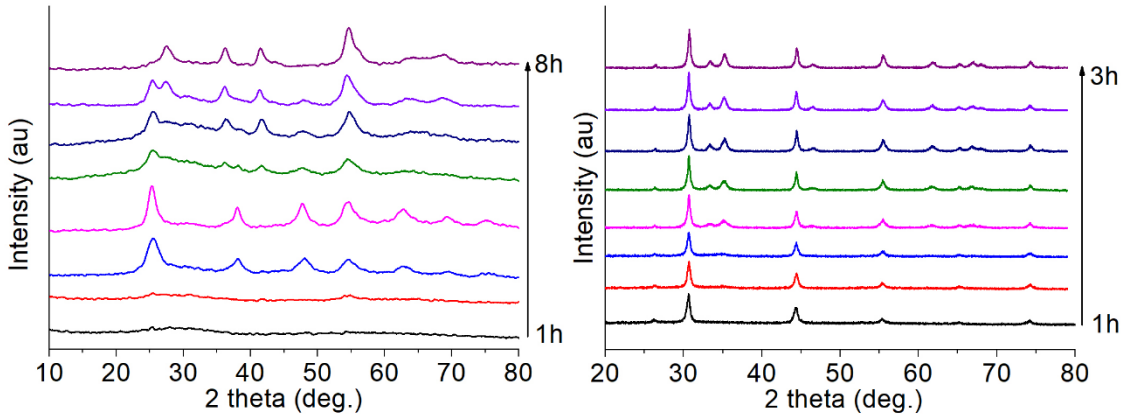

Fig.2: XRD pattern of the as-milled TiO_2 and ZnO samples.

As a result, all titanate sources were suitable for the production of $ZnTiO_3$. Among the grinding parameters, the speed and the number of grinding balls were varied, and several grinding vessels made of different materials were tested. It has been found that a grinding vessel

made of a material of inappropriate density, low speed and ball speed are not suitable for the production of ZnO and $ZnTiO_3$. The same was observed for $NaNbO_3$ and $BaTiO_3$. The high grinding speed and high wear-rate material contaminate our sample, destroying the perovskite structure. After the successful production of $ZnTiO_3$, since the ultimate goal is to determine a general mechanochemical perovskite synthesis, we also tried to generate additional perovskites based on the obtained results. Thus, Mn / Sn / $PbTiO_3$ perovskites were successfully prepared from $MnCl_2$, $SnCl_2$, $PbCl_2$ and $TiCl_4$ precursors. The above materials were also co-milled and prepared from the corresponding metal oxide by a two-step technique.

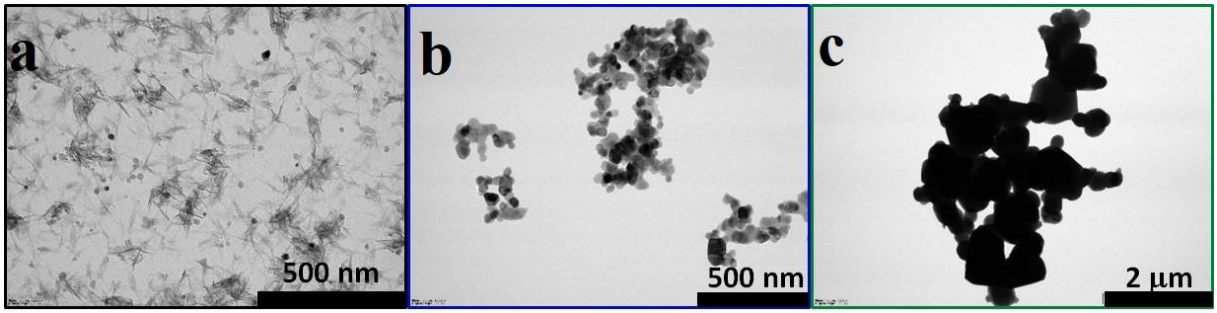

Fig.3: TEM images of $ZnTiO_3$ samples calcined at different temperature (a: non calcined; b: 400 °C; c: 1000 °C)

Conclusion

We have successfully used the high-energy milling to produce perovskite-structured materials and metal-oxide samples. Our proposed conversion from the pressure measured in the closed grinding vessel proved to be correct, which was supported by XRD and TG measurements. The use of milling drums made of different materials was successfully coordinated using the equation we proposed earlier to determine the grinding energy.

Acknowledgements

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