Available online at www.sciencedirect.com
SCIENCE DIRECT®

Thermochimica Acta 445 (2006) 23–26

thermochimica acta

www.elsevier.com/locate/tca

Unprecedented formation of metastable monoclinic $BaCO_3$ nanoparticles

Reto Strobel [a,b], Marek Maciejewski [b], Sotiris E. Pratsinis [a], Alfons Baiker [b,*]

[a] Particle Technology Laboratory, Department of Mechanical and Process Engineering, ETH Zurich, Sonneggstrasse 3, CH-8092 Zurich, Switzerland
[b] Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Hönggerberg, HCI, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

Received 24 January 2006; received in revised form 14 March 2006; accepted 19 March 2006
Available online 27 March 2006

Abstract

Barium carbonate nanoparticles (50–100 nm) were prepared by flame spray pyrolysis. The rapid quenching during the preparation process resulted in the unprecedented formation of pure monoclinic $BaCO_3$. The as-prepared materials were characterized by electron microscopy, X-ray diffraction as well as by thermogravimetric and differential scanning calorimetric analyses. At ambient conditions the metastable monoclinic phase transformed easily into the thermodynamically stable orthorhombic $BaCO_3$ (witherite) within a few days.

Keywords: Flame spray pyrolysis; Barium carbonate; Nanomaterials; Crystal structure

1. Introduction

Witherite (orthorhombic $BaCO_3$) occurring in nature and formed during conventional precipitation synthesis is the only stable phase of $BaCO_3$ at room temperature. Before complete decomposition into BaO the orthorhombic form undergoes transitions into a hexagonal phase at ca. 810 °C and into a cubic form around 980 °C [1–4]. Additionally, monoclinic $BaCO_3$ stabilized by a partial anion substitution of $CO_3{}^{2-}$ in the host lattice by $SO_4{}^{2-}$ is accessible by rapidly quenching a mixture of $BaCO_3$ and $BaSO_4$ from 800 °C into liquid nitrogen [5]. The metastable monoclinic phase was also observed for $BaCO_3$ particles supported on Al_2O_3 as applied in nitrogen oxides storage-reduction (NSR) catalysts [6]. Here, flame spray pyrolysis (FSP) was used for the synthesis of pure $BaCO_3$ nanoparticles. FSP is usually applied for the preparation of metal and metal-oxide nanoparticles [7,8]. Recently it has been shown that also nanosized salts such as carbonates, phosphates and halogenides can readily be made by flame synthesis [9–11].

2. Experimental

2.1. Powder preparation

Barium carbonate was prepared by flame spray pyrolysis, using barium (II) 2-ethylhexanoate (75% in 2-ethylhexanoic acid, Alfa Aesar, 99.8%) dissolved in ethanol (Alcosuisse, 98%) as precursor (Ba concentration, 0.2 M). The liquid mixture was fed at 5 ml/min into a spray nozzle, dispersed by oxygen (5 l/min, pressure drop 1.5 bar at capillary tip) and ignited by a surrounding premixed methane/oxygen flame [12]. The as-prepared particles were collected on a glass fibre filter by the aid of a vacuum pump.

2.2. Powder characterization

The specific surface area was determined according to the BET method on a Micromeritics Tristar. The BET particle diameter (d_{BET}) was calculated according to $d_{BET} = 6/(SSA \times \rho)$, where SSA and ρ stand for the specific surface area and density, respectively. XRD analysis was carried out on a Siemens D5000 powder X-ray diffractometer between 16 and 65° 2Θ with a step of 0.01° and 2 s/step. For transmission electron microscopy (TEM), the material was dispersed in ethanol and deposited onto a perforated carbon foil supported on a cop-

---

[*] Corresponding author. Tel.: +41 44 632 315; fax: +41 44 632 1163.
E-mail addresses: alfons.baiker@chem.ethz.ch, baiker@chem.ethz.ch (A. Baiker).

0040-6031/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2006.03.020

per grid. The investigations were performed on a CM30 ST (Philips, LaB6 cathode, operated at 300 kV). Thermal analysis (TA) combined with mass spectrometry (MS) was carried out on a Netzsch STA 409 thermoanalyzer. The thermogravimetric (TG) and differential scanning calorimetric signals (DSC) were recorded during heating with a rate of 10 °C/min in the atmosphere of pure Ar (flowing rate 50 ml/min). The composition of the gas phase was monitored by the OmniStar (Pfeiffer Vacuum) quadrupole mass spectrometer connected to the thermoanalyzer. The amount of evolved CO_2 resulting from the evolution of adsorbed species was determined by PulseTA technique by the comparison of the integral intensity of the CO_2 ($m/z = 44$) with the integral intensities of 1 ml pulses of CO_2 injected after total decomposition of the sample [13]. Three as-prepared samples were calcined with a rate of 10 °C/min to 600, 261 and 102 °C, respectively, and after fast cooling analyzed by XRD.

3. Results and discussion

The as-prepared material consisted of non-agglomerated crystalline $BaCO_3$ nanoparticles (Fig. 1). TEM analysis further revealed the formation of “bean-like” shaped particles with length of about 100 nm and width of approximately 50 nm. The corresponding BET-particle diameter for a spherical particle was 70 nm (specific surface area (SSA): 20.5 m^2/g) in good agreement with the TEM observations. Fig. 2A depicts the XRD pattern of as-prepared $BaCO_3$ 1 h after its preparation. Crystalline, monoclinic $BaCO_3$ was observed with only traces of the stable orthorhombic form and no BaO could be detected. The electron diffraction pattern (inset, Fig. 1) revealed, however, the presence of orthorhombic $BaCO_3$ indicating that the monoclinic phase is not preserved during TEM analysis and rapidly transformed into orthorhombic $BaCO_3$.

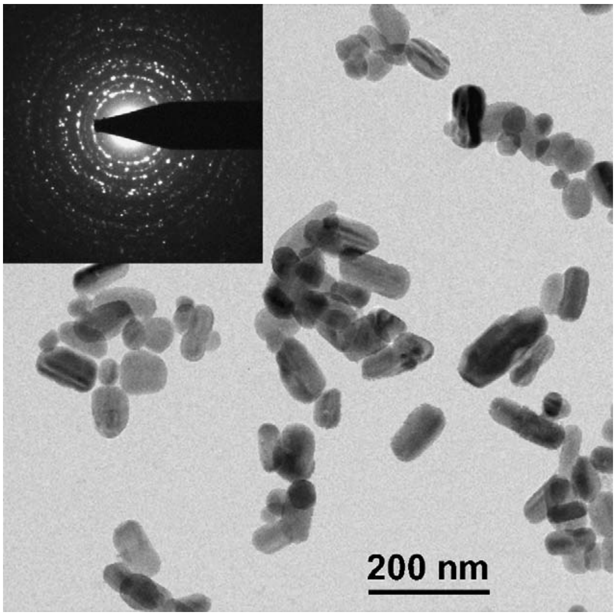

Fig. 1. Transmission electron micrograph of flame-made $BaCO_3$ nanoparticles. The inset depicts the corresponding electron diffraction pattern.

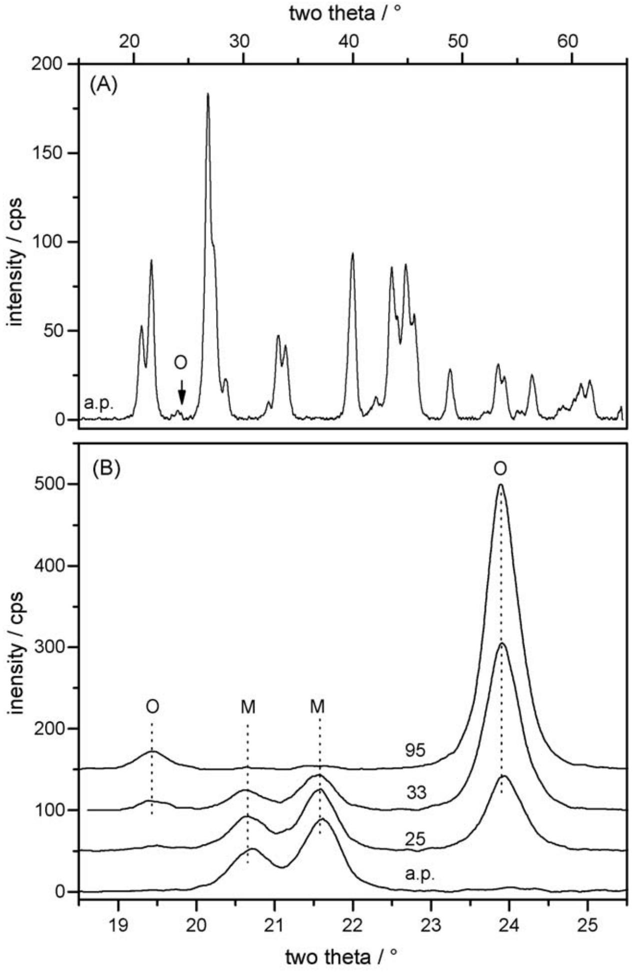

Fig. 2. (A) XRD pattern of as-prepared (a.p.) $BaCO_3$. The unlabeled reflections belong to the monoclinic $BaCO_3$. Only traces of the orthorhombic phase (O) were detected. (B) XRD patterns of $BaCO_3$ as a function of time (marked in hours on the curves). Within 95 h complete transformation of monoclinic (M) to orthorhombic (O) $BaCO_3$ takes place.

As $BaCO_3$ would not be stable and decompose into BaO and CO_2 at the high temperatures in the flame, it can be assumed that in a first step BaO particles are formed. Later downstream at lower temperatures and exposed to a significant amount of CO_2 from the combustion process BaO transforms into $BaCO_3$. At 1300 °C the equilibrium CO_2 partial pressure for the reaction $BaO + CO_2 \leftrightarrow BaCO_3$ would be 0.1 bar, a reasonable value for CO_2 in the flame [14]. A temperature of 1300 °C is reached at about 15 cm above the nozzle [12]. The formation of $BaCO_3$ instead of BaO in the flame process is not surprising as flame synthesis resulted also in the formation of $CaCO_3$ [10], which would decompose into CaO at even lower temperatures than $BaCO_3$ [14].

Table 1 depicts the unit cell parameters for flame-made, monoclinic $BaCO_3$ in comparison with the data reported for $SO_4{}^{2-}$ stabilized monoclinic $BaCO_3$ [5]. Despite the smaller cell volume of 154.89 Å^3 instead of 158.32 Å^3, the crystal structure was the same. The absence of larger $SO_4{}^{2-}$ groups in the crystal structure leads to smaller unit cell volume. At ambient conditions the monoclinic phase transformed into the orthorhombic

Table 1
Crystal data for monoclinic $BaCO_3$

$BaCO_3$ (flame-made):	$a = 6.863$, $b = 5.276$, $c = 4.520$ Å $\beta = 108.89°$, $V = 154.89$ Å^3 $Z = 2$, $P2_1/m$
SO_4^{-2} stabilized $BaCO_3$ [a]:	$a = 6.913$, $b = 5.295$, $c = 4.545$ Å $\beta = 107.89°$, $V = 158.32$ Å^3 $Z = 2$, $P2_1/m$

[a] From Nishino et al. [5].

$BaCO_3$ (Fig. 2B). Fig. 3 shows the detailed evolution of this transformation by monitoring the intensity of monoclinic and orthorhombic reflections of $BaCO_3$. Exposed to air at room temperature the monoclinic $BaCO_3$ completely transformed into the orthorhombic form within 4 days.

Thermogravimetric and differential scanning calorimetric results of as-prepared $BaCO_3$ are shown in Fig. 4. The amount of CO_2 evolved during decomposition of $BaCO_3$ into BaO in the range 800–1350 °C was determined by quantification of the $m/z = 44$ signal. The amount of CO_2 was equivalent to 99.3% of the stoichiometric amount of CO_2 in the sample. Three endothermal events were observed on the DSC curve. The first and the second originate from the polymorphic transformation of the orthorhombic into hexagonal phase (818 °C) followed by the transformation of hexagonal into cubic phase (981 °C) [1,2]. The peak at 1123 °C indicates the maximal rate of the endothermic barium carbonate decomposition. No distinct DSC signal was observed for the transformation of monoclinic into the orthorhombic phase. The XRD analysis of monoclinic $BaCO_3$ after heating up to 600, 261 and 102 °C, respectively, has shown that already upon heating to 102 °C only orthorhombic and no monoclinic $BaCO_3$ could be observed by XRD (Fig. 4B). This shows clearly the very unstable nature of the monoclinic phase. The unique formation of this phase is traced to the rapid quenching of the flame-made particles undergoing a steep temperature profile from ca. 2000 °C down to 300 °C within a few milliseconds [7,12]. In contrast in the conventional preparation process via precipitation the stable orthorhombic $BaCO_3$ is formed [1–4].

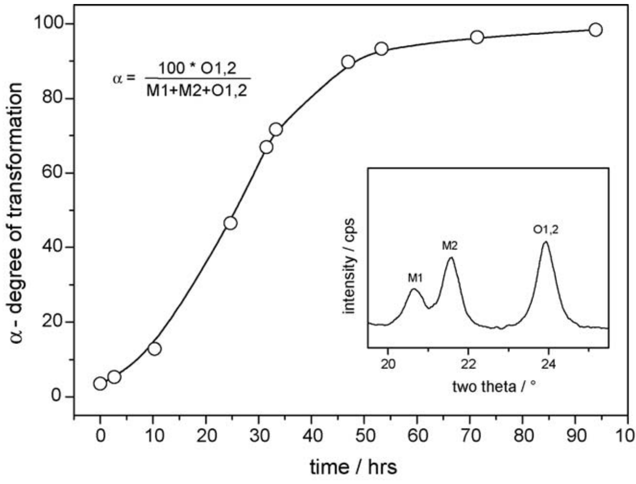

Fig. 3. Degree of the transformation of monoclinic into orthorhombic barium carbonate. The degree α was calculated using the integral intensities of two monoclinic (M1, $d = 4.2534$ Å, and M2, $d = 4.1166$ Å) and two orthorhombic (O1, $d = 3.7236$ Å, and O2, $d = 3.6604$ Å) reflections.

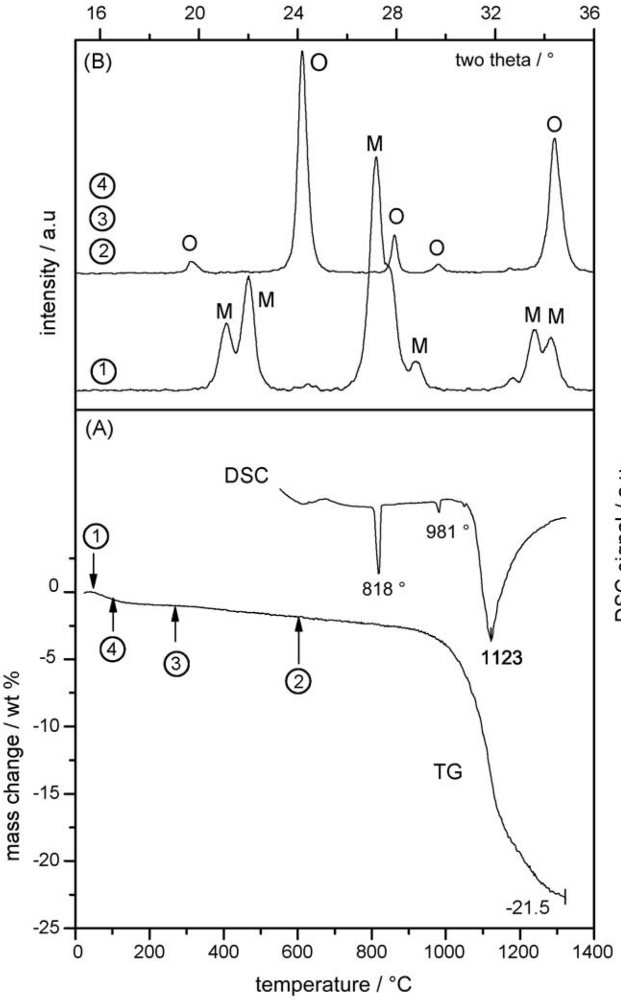

Fig. 4. Thermal analysis and XRD investigations of monoclinic $BaCO_3$. (A) Change of the mass (TG) and thermal effects (DSC) recorded during heating of $BaCO_3$ in Ar with a rate of 10 K/min. The samples analyzed later by XRD were collected after separate runs stopped at 600 (2), 261 (3) and 102 °C (4). (B) XRD patterns of $BaCO_3$ heated up to the temperatures marked on TG curve.

4. Conclusions

Monoclinic $BaCO_3$ nanoparticles (50–100 nm) were prepared by flame spray pyrolysis. As a result of the rapid quenching during the flame synthesis process, monoclinic $BaCO_3$ was formed without the addition of any stabilizing sulphate anions. At ambient conditions the monoclinic phase transformed into orthorhombic $BaCO_3$ within 4 days. Although no distinct DSC signal could be observed for this transformation, only orthorhombic $BaCO_3$ was found after heating the powder up to 100 °C.

Acknowledgments

We thank Dr. Frank Krumeich (ETH) for the TEM measurements and Dr. Michael Wörle (ETH) for calculating the unit cell parameters. Financial support by ETH Zurich (TH 2/03-2) is kindly acknowledged.

References

[1] I. Arvanitidis, D. Sichen, S. Seetharaman, Metall. Mater. Trans. B 27B (1996) 409.
[2] C.M. Earnest, Thermochim. Acta 137 (1989) 365.
[3] J.J. Lander, J. Chem. Phys. 17 (1949) 892.
[4] K.O. Stromme, Acta Chem. Scand. A A29 (1975) 105.
[5] T. Nishino, T. Sakurai, N. Ishizawa, N. Mizutani, M. Kato, J. Solid State Chem. 69 (1987) 24.
[6] L. Lietti, P. Forzatti, I. Nova, E. Tronconi, J. Catal. 204 (2001) 175.
[7] L. Mädler, KONA 22 (2004) 107.
[8] S.E. Pratsinis, Prog. Energy Combust. Sci. 24 (1998) 197.
[9] R.N. Grass, W.J. Stark, Chem. Commun. (2005) 1767.
[10] M. Huber, W.J. Stark, S. Loher, M. Maciejewski, F. Krumeich, A. Baiker, Chem. Commun. (2005) 648.
[11] S. Loher, W.J. Stark, M. Maciejewski, A. Baiker, S.E. Pratsinis, D. Reichardt, F. Maspero, F. Krumeich, D. Günther, Chem. Mater. 17 (2005) 36.
[12] L. Mädler, H.K. Kammler, R. Mueller, S.E. Pratsinis, J. Aerosol Sci. 33 (2002) 369.
[13] M. Maciejewski, C.A. Müller, R. Tschan, W.D. Emmerich, A. Baiker, Thermochim. Acta 295 (1997) 167.
[14] K.H. Stern, E.L. Weise, Nat. Stand. Ref. Data Ser. 30 (1969) 1.