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Flying droplets as model system for spray drying—An *in situ* synchrotron X-ray scattering study on complex oxides catalyst precursors

Jork Leiterer [a], Franziska Emmerling [a,*], Jörg Radnik [b,**], Ursula Bentrup [b], Angelika Brückner [b]

[a] BAM Federal Institute of Materials Research and Testing, Richard-Willstätter-Str. 12, 12489 Berlin, Germany
[b] Leibniz-Institut für Katalyse, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

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ABSTRACT

As a model for spray drying the early stages of crystallization of complex molybdate catalyst precursors were monitored online in droplets levitated acoustically. Synchron X-ray scattering techniques were applied to study the drying process of a typical molybdate catalysts precursor prepared from Ni-,Fe-,Bi-nitrate, ammonium heptamolybdate and H_3PO_4. Comparison with diffraction patterns obtained from sessile droplets shows significant differences in the crystal growth, whereas the final crystal structure – including a Keggin-type anion – is identical in both cases. The levitated samples exhibit a decelerated growth with a large number of small crystallites at the beginning of the crystallization, whereas in case of the sessile droplets a small number of large crystallites were observed after a few minutes. The acoustic levitation using an ultrasonic trap proves to be an elegant tool to mimic spray drying and offers new possibilities in relation to the understanding of the drying process.

1. Introduction

Molybdate containing mixed metal oxides are widely applied as catalysts in heterogeneous selective oxidation processes [1,2]. In industry, such catalysts are frequently prepared by slurry procedures comprising a series of subsequent steps including precipitation, isolation of the precipitate, spray drying and final calcination. Tailoring the different preparation steps for the preferential formation of desired precursor and catalyst phases would be highly desirable but is mostly difficult to realize, since a sound understanding of the different preparation steps is still missing. Thus, the preparation method, the nature of the used components and the reaction conditions play an important role and affect the final composition, structure and performance of the catalytic material. To optimize the synthesis strategies of such complex oxides, particularly in terms of an enhanced and reproducible performance of the catalysts, a deeper insight into the synthetic process by *in situ* methods is inevitable.

Recently, we reported on simultaneous wide- and small-angle X-ray scattering (WAXS/SAXS) and Raman spectroscopic experiments at the μSpot Beamline (BESSY, Berlin) enlightening the precipitation of certain phases in the liquid phase synthesis of molybdate catalyst precursors [3]. These investigations in the complex system ammonium heptamolybdate (AHM)/Ni-,Fe-,Bi-nitrate/HNO_3/H_3PO_4 showed that after the addition of the mixed metal nitrate solution to the solution of AHM, a crystalline precipitate is immediately formed indicated by the respective Bragg reflections. The precipitate alters after the addition of H_3PO_4, loses its crystallinity and partly dissolves, respectively, at higher temperature. At the end of the experiment no Bragg reflections were detected. The existence of Keggin-type ions could be verified by Raman spectroscopy. If the slurry was spray-dried, the formation of a crystalline phase with cubic symmetry consisting of Keggin ions could be observed.

Obviously, the drying procedure leads to crystallization. Only few investigations on the influence of the drying methods on the catalytic performance and no *in situ* studies to our best knowledge are known. It was reported by Lin [4], that starting from Mo–V–Te–Nb oxide precursors with identical composition, the powder pattern of the dried samples differ depending on the applied drying method (heat evaporation and freeze-dry) [4]. Reflecting the structural differences, the respective catalyst performance varies, too. However, further information about the early stages of drying, especially the crystallization process during the whole drying period, was not given.

In situ investigations of spray-drying processes are very rare. First attempts were made by Sen et al. [5] applying a mobile spray dryer at a synchrotron beamline [5]. The authors derived information on the particle formation probing different temperature zones. The suitability of the acoustic levitation to imitate the condition during the spray-drying was discussed in the literature [6,7]. Particularly, former investigations on the evaporation

* Corresponding author. Fax: +49 30 8104 1137.
** Corresponding author. Fax: +49 381 1281 51308.
E-mail addresses: franziska.emmerling@bam.de (F. Emmerling), joerg.radnik@catalysis.de (J. Radnik).

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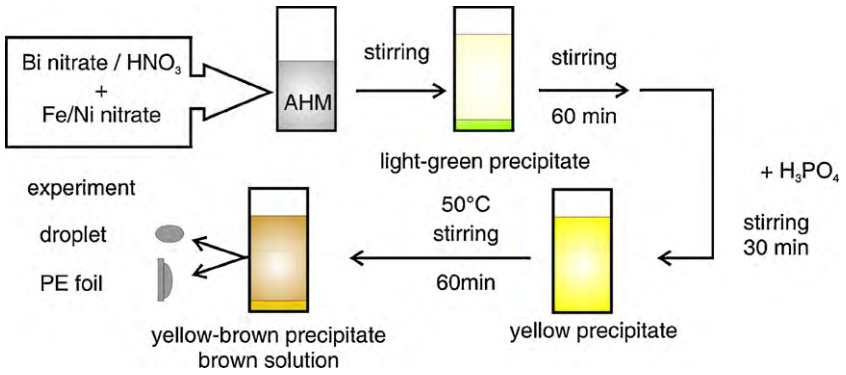

Fig. 1. Preparation flow chart.

kinetics of pharmaceutical proteins suggest that an acoustic levitator can be used as a model system for spray drying [6,8].

Previously, we have used an acoustic levitator to investigate the crystallization processes of small molecules and proteins [9–11]. The objective of this study is to explore, whether the spray drying process of a typical catalyst synthesis mixture containing AHM, Ni, Fe and Bi nitrate, HNO_3 and H_3PO_4 can be modelled and monitored by trapping slurry droplets in an ultrasonic levitator. To gain a deeper insight into the drying process, *in situ* X-ray scattering investigations were performed.

2. Experimental

2.1. Sample preparation

A typical slurry used in the experiments was prepared as already described [3] and is displayed in Fig. 1. The composition of the mixture was chosen to mimic the complexity of catalysts typically used. 25 mL aqueous solution of 11.63 g $Ni(NO_3)_2{\cdot}6H_2O$, 4.04 g $Fe(NO_3)_3{\cdot}9H_2O$ and 4.86 g $Bi(NO_3)_3{\cdot}5H_2O/HNO_3$ were added to 24.72 g AHM in 75 mL H_2O. After one hour stirring 2.5 mL 85 wt.% H_3PO_4 were added. This slurry was stirred for further 30 min and afterwards heated up to 50 °C. At this temperature the mixture was stirred for one hour.

2.2. In situ experiments

In a typical experiment one droplet of this solution with a volume of 2.5 μL was directly hand-injected into the ultrasonic levitator by means of a microlitre pipette (0.5–10 μL, Eppendorf, Germany) and irradiated by the X-ray beam (100 μm in diameter, $E = 11.94$ keV, $\Delta E/E \approx 10^{-4}$, $\lambda = 0.10386$ nm). Acoustic levitation allows a stable positioning of sample volumes from 5 nL to 5 μL without influence from solid container walls. An ultrasonic trap (Tec5, Oberursel, Germany) was implemented at a micro focus beamline (Fig. 2, further information on the beamline can be found in ref. [12]). Applying this setup, the monitoring of tiny sample amounts in an acoustically levitated droplet is possible. Scattered intensities were collected 20 cm behind the sample with a two-dimensional X-ray detector (MarMosaic, CCD 3072 × 3072 pixel and a point spread function width of about 100 μm). The same experiment was repeated on sessile droplets deposited on PE foil. A turnable microscope was used in its in-beam-position to align the sample precisely at the X-ray micro spot. During the experiment the sample was observed in an off-beam-position. Interference from scattered radiation leads to smooth diffraction rings around the beam axis (Debye–Scherrer rings [13]). These scattering images were converted by algorithm of the software FIT2D [14] into diagrams of scattered intensities as a function of the scattering vector q, defined as $q = 4\pi/\lambda \sin\theta$, where 2θ is the scattering angle between incident and scattered photons and λ the wavelength. Due to the small incident beam diameter no mathematical correction of the experimental scattering function was needed. In the case of a levitated droplet, the scattering from pure solvent was used to estimate the background contribution.

3. Results and discussion

In Fig. 3 the recorded scattering curves of a levitated droplet of slurry are shown. Each pattern was collected with an irradiation time of 10 s during 60 min of levitation. Fig. 3 shows the first 24 min of levitation, starting from the top to the bottom curve.

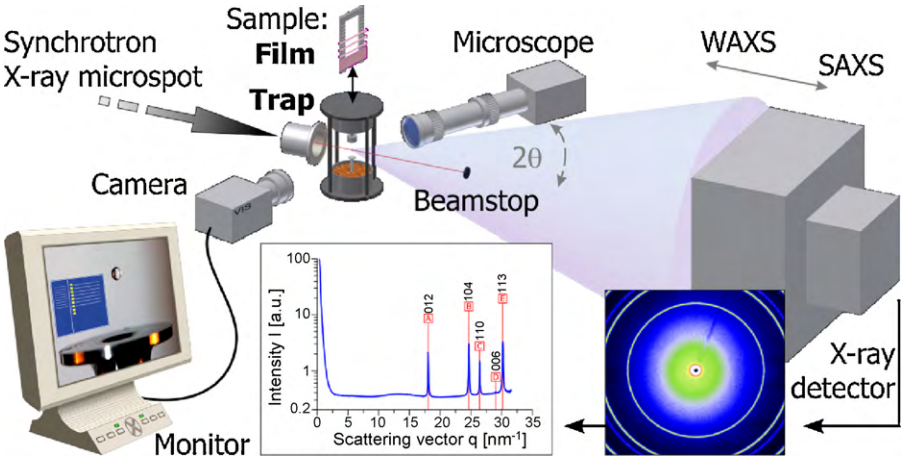

Fig. 2. Experimental implementation of an acoustic levitator (trap) for X-ray scattering. Switchable sample holders (a) trap, and (b) film.